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RESEARCH PERSPECTIVES

ABSTRACTS OF Ph. D. THESES 1984

PART II
SCIENCE

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कृपया पुस्तक के ऊपर कोई निशान आदि
न लगायें।

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पुस्तकालय

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वर्ग संख्या 016 BAN-R.2 आगत संख्या 6557

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RESEARCH PERSPECTIVES

(Abstracts of Ph. D. Theses—1984)

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PART II

(SCIENCE)

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Cover Design : Prof. A. P. Gajjar

Price : Rs. 150/-

Published by O. P. Tandon, Officer on Special Duty, Banaras Hindu University, Varanasi (India) and Printed at the Ratna Printing Works, Kamachha Varanasi-221010.

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R. P. RASTOGI
VICE-CHANCELLOR

BANARAS HINDU UNIVERSITY
VARANASI - 221005

Foreword

I am happy to note that Pt. II of Research Perspectives—Abstracts of Ph. D. These (1984) covering the research done in the Science Sector is in our hands. This series of publications has generated academic interest all over the country and many Universities and Institutions of Higher Learning have responded positively to this contribution of the Banaras Hindu University. The Officer on Special Duty (Acad. & Exams.), the University Librarian and the members of the Documentation Centre deserve appreciation for the services rendered by them in bringing out the results of enormous research conducted in this University, year after year.

I am sure that this useful work will be continued and our great national Institution will be setting the pace in this direction as well. I hope that Pt. I of this volume pertaining to Humanities Sector will also be brought out soon.

R. P. Rastogi

Vice-Chancellor

Varanasi
March 30, 1988

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Editorial Note

The second volume of Research Perspectives containing Abstracts of Ph. D. Theses—1984, covers the abstracts of theses submitted in the Faculties of Agriculture, Engineering and Technology, Indian Medicine, Medicine and Science. This arrangement has been made to distribute the volume of work in a more meaningful and useful manner besides managing the physical aspect of this annual research contribution.

The profound academic interest taken by Prof. R. P. Rastogi, Vice-Chancellor, Banaras Hindu University in enriching the academic life continues to draw us to greater commitment in contributing our mite towards this cause.

The entire compilation work has been done by the Documentation Unit of the Central Library, B.H.U. under the overall supervision of Sri H.D. Sharma, the University Librarian. I take this opportunity to record my gratefulness for their help in this publication. As on previous occasions, I have received cooperation and assistance both from the colleagues in the administration and some of the University dons. Shri S. P. Mukherjee, Deputy Registrar and Shri R. B. Agrawal, Assistant Registrar in the Academic Section and Shri D. P. Bhattacharya and Sri S. S. Rahman in the Controller of Examinations' Office have rendered valuable assistance and I am very grateful to them.

My thanks are also due to M/S. Ratna Printing Works for printing this volume.I have no words to express my appreciation of the understanding shown by my family members inspite of my many failings.

O. P. TANDON

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Faculty of Agriculture

AGRICULTURAL ECONOMICS

ECONOMICS OF VEGETABLE CULTIVATION IN SEWAPURI BLOCK, VARANASI DISTRICT, U. P.

R. P. Maurya Sup : *Dr. M. M. Bhalerao*

Vegetables have not received due attention from the researchers and planners in India. Consequently, vegetables are a luxury for a majority of India's population because of their short supply and higher prices. It is, therefore, imperative to conduct micro studies into the economics of vegetable production particularly because of their low consumption per capita inspite of their importance in the balanced diet as suppliers of rich vitamins, proteins, minerals etc. The present study is an attempt in this direction.

Objectives :

Objectives of the study are :

(i) to examine the share of ten vegetables in the gross cropped area, human labour employment as well as gross income of the farmers by size of farm,

(ii) to study the output input relationship as well as the various measures of farm profit in vegetables by size of farm,

(iii) to examine the efficiency of resource use in vegetables by size of farm,

(iv) to examine the cost price relation in vegetables both for bulk line cost and average cost of production; and

(v) to estimate the marketing charges and the share of product in the consumer's rupee in vegetables.

Hypotheses :

Following hypotheses have been tested in the thesis :

(1) Percentage share of vegetables in the total human labour employment and gross income of farmers is much higher than their share in the gross cropped area,

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(2) Percentage share of vegetables in the gross cropped area, human labour employment on the farm as well as in the gross income of the farmers decrease with the increase in the size of farm,

(3) Bulk line cost covers greater proportion of farmers, area and output of vegetables than the average cost and the proportion of harvest price covered by the bulk line cost is higher than that covered by average cost of production of vegetables,

(4) The output input ratio, farm business income, family labour income and net income per hectare for vegetables decrease with the increase in the size of farm,

(5) Resource use in vegetable production is not efficient and there is considerable scope for increasing the resource productivity in vegetables; and

(6) There is also considerable scope for increasing the share of producer in the consumer's rupee for vegetables.

Sampling Design

1. Selection of villages

A list of all villages from Sewapuri Block was prepared in descending order of the percentage of area under vegetables to gross area sown, and from this list first ten villages were selected for study.

2. Selection of farmers :

A list of all the vegetable growers (i. e. growing at least one vegetable) from the ten selected villages was prepared in ascending order of the size of their owned holding and divided into three strata viz. below 1.00 hectare; 1.00 to 2.00 hectare and 2.00 hectares and above.

Five farmers from each of the three size groups per village, were then selected at random. Thus the study covered a total of 150 farmers with 15 farmers per village or 50 farmers per size group.

Method and Period of Enquiry

Survey method was used for the collection of data which relate to the period from 1st July 1980 to 30th June, 1981.

Analytical Tools :

1. For the ten vegetables under study both bulk line cost as well as average cost of production per hectare and per quintal have been estimated with the help of graphs and by computing averages for the three size groups and for the sample as a whole.

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2. For the estimation of productivity of resources, Cobb-Douglas production function has been used for the ten vegetables, for three size-groups (small, medium and large) as well as for the sample as a whole. *Thus forty functions in all have been fitted.* Five independent variables namely land in hectares (X_1), Cost of seed in Rs. (X_2), Cost of manures and fertilizers in Rs. (X_3), human labour in mandays (X_4) and cost of irrigation in Rs. (X_5) and the dependent variable namely gross value of product in rupees, have been used in the production function.

The efficiency of resource use for the five independent variables has been measured by the ratio of marginal value product to marginal cost (MVP/MC).

Results :

The total population of Sewapuri block is 93950 with an area of 17010 hectares. Soils of the block vary from clay to sandy loam. The main crops of the block are paddy, wheat, arhar, bajra and sugarcane. Vegetables occupy 4.94% of the gross area sown. Average annual rainfall of the block is 105 cm. About 35% of the gross cropped area in the block is (gross) irrigated. Main sources of irrtgation are wells and tubewells.

For sample farmers, average size of owned holding was 1.77 hectares. Main crops grown by the sample farmers were wheat, paddy, sugarcane, arhar, maize, bajra, and vegetables. Intensity of cropping was 176.18% About 43% of the gross area sown of the sample farmers was irrigated.

Distribution of total cost on various inputs, indicates that in all the ten vegetables, namely potato, tomato, onion, cauliflower, brinjal, ladys finger, pea, cucumber, sponge gourd and bitter gourd, human labour (family as well as hired) accounts for the highest share (except the cost of seed in case of pea and potato) in the cost followed by rental value of owned land, fertilizers and manures, irrigation, bullock labour and seed.

The inter vegetable comparison of cost shows that potato has the highest cost of cultivation per hectare followed by pea, onion, cauliflower brinjal, sponge gourd, tomato, ladys finger and bitter gourd.

Onion gives maximum net income per hectare followed by cauliflower, tomato, bitter gourd, cucumber, pea, sponge gourd, potato, brinjal and ladys finger.

In all the ten vegetables bulk line cost covered greater proportion of farmers output, as well as area and also greater proportion of the respective prices of the ten vegetables under study than that covered by the average cost of production.

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The functional analysis shows that there is considerable scope for increasing the productivity of the five resources studied.

The producers share in the consumers rupee ranged between 62.05% for tomato to 66.80% for brinjal in case of Chandwa market and from 61.05 percent in case of tomato to 66.50 percent in case of brinjal for Kamachha market.

Finally, the results indicated that hypotheses number one, three, five and six were accepted while hypothesis number four was partially accepted only in the following cases :—

(i) For net income in case of potato, onion, cauliflower, ladys finger and cucumber,

(ii) For farm business income and family labour income in all the vegetables except tomato, and

(iii) For output input ratio only in case of ladys finger.

A STUDY OF COOPERATIVE MARKETING SOCIETIES IN INDIA

Ramashray Singh Sup : *Dr. M. M. Bhalerao*

India is predominantly rural and about 70 per cent of our population depends on agriculture. Almost half of our population lives below the poverty line and the three decades of planning have witnessed considerable efforts for rural development, which mainly depends on agricultural development. Rairing the productivity and incomes of the farmers is a prerequisite for rural development. Marketing imperfections inhibit rural development by putting hurdles in the way of providing reasonable price to the producer at the same time satisfying the needs of the consumer. Cooperative Marketing Societies have been organised in the country mainly to reduce the long chain of middlemen and provide an efficient marketing service. These societies however, suffer from a number of shortcomings such as inadequate coverage, weak financial structure, poor business, lack of loyalty from members, lack of technical and managerial personnel competition from vested interests and uneven development in different regions etc. Assessment of their performance is therefore, necessary. The present study is an attempt in this direction.

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Objectives :

Objectives of the study are :

1. to assess the progress of cooperative marketing societies in India over the decade 1969-1978 at the National level, State level and District level i.e. the National Agricultural Cooperative Marketing Federation (NAFED), State Cooperative Marketing Federations and District Marketing Societies with special reference to their number, membership, financial resources, credit, storage, distribution and marketing activities;
2. to analyse the growth of cooperative primary marketing societies in India over the decade 1969-78, with special reference to their number, membership, financial resources, credit, storage, distribution and marketing activities;
3. to study the interested inequality in the growth of primary marketing societies with regard to the above variables over the decade 1969-78;
4. to study the factors affecting quantity of agricultural produce of the members, marketed by primary marketing societies;
5. to isolate the factors contributing to the success or failure of the primary marketing societies in different states of India and to suggest measures for their improvement so as to make them an effective instrument of rural development.

Scope and Period of Study :

The study is limited mainly to the general purpose marketing societies at the primary level i. e. Primary Marketing Societies (PMS). The period of the study is the decade 1969-78. Since comparable data for the major 17 states are available for this period and this decade, almost coinciding with the fourth and fifth plans, has witnessed considerable growth of marketing societies.

Data Sources :

The study is based on the secondary data compiled from the publications of the Reserve Bank of India, Directorate of Economics and Statistics, Government of India, National Sample Survey, Central Statistical Organisation, National Cooperative Union of India, National Cooperative Development Corporation and International Cooperative Alliance.

Analytical and Statistical Tools :

The trends in the performance of Marketing cooperatives have been studied by computing the indices for the decade with 1968-69 = 100 for various indicators of cooperative marketing development.

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Correlation technique is used to study the relation between cooperative development and general agro-economic development. Student 't' test is used to evaluate the significance of correlation coefficient.

Production function analysis (Cobb-Douglas function) is used to study the impact of various factors on the quantity of produce of members marketed Primary Marketing Societies.

The trends and extent of interstate ineqality in the performance of Primary Marketing Societies are analysed with the help of :

(i) Coefficient of variation,

(ii) Ginni Coefficient of concentration and

(iii) Lorenz Curves.

Hypotheses :

Following hypotheses have been tested in the thesis :

(1) Primary Marketing Societies in India have made considerable progress in their financial resources and storage activities only,

(2) Primary Marketing Societies in India have failed to make any significant progress in their credit, marketing, distribution and linking of credit with marketing activities,

(3) There exists considerable interstate inequality in the performance of P. M. S. in 17 major states of India but this inequality has decreased during the decade 1969-78.

(4) Quantity of agricultural produce sold by PMS in India is influenced by :

(i) Short-term credit supplied by Primary Agricultural Credit Societies (PACS).

(ii) Medium term Credit Supplied by Primary Agricultural Credit Societies (PACS).

(iii) Long-term credit supplied by Land Development Banks (LDBs).

(iv) Value of sales as owners by PMS.

(v) Owned storage capacity of PMS.

(vi) Loans advanced by PMS.

(vii) Proportion of regulated markets to total markets.

(5) Performance of PMS in the 17 states is influenced by the overall agro-economic development in these states.

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Results

The performance of one national level (NAFED), 29 state level, 380 district level and 3592 primary level marketing cooperatives in India in 1978 is a sad commentary on the otherwise rosy picture of cooperative credit. Of these primary societies, 28 66 were general purpose marketing societies with 28.84 lakh individual members and 1.45 lakh society members while others were special commodity societies like the sugarcane marketing, societies, cotton marketing societies, fruit societies, etc. Average individual membership per society was 936.

During the decade 1969-78 they made considerable progress quantitatively, unfortunately unaccompanied by qualitative improvement. Thus the present study indicates that in these general purpose MMS marketed 1978 agricultural produce worth Rs. 328.86 crores and agricultural requisites worth Rs. 317.28 crores along with consumer goods worth Rs. 236.80 crores.

However, unfortunately average business per society (PMS) hardly reached Rs. 5 lakhs which was much below the standard norm of viability of Rs. 30 lakhs recommended by the Dantwala Committee on Cooperative Marketing in 1966. Thus they accounted for less than 10 per cent of the marketed surplus of agricultural producers in the country.

They made considerable progress during the decade 1969-78 in their financial resources and owned storage capacity, but still their financial structure was weak and storage capacity inadequate which was hardly 7 million tonnes, i.e. less than one third of the total buffer stocks expected to be built up by the public sector institutions. Less than 3/4th of these societies were state partnered and owned godowns. Hardly 37 per cent of them advanced loans while almost same numbers hired godowns. Hardly 64% undertook marketing activities, 59% distribution of farm requisites, 61% distribution of consumer goods and only 14% recovered loans of credit societies, to the tune of hardly 17% of the total loans recovered by all cooperatives. The tragedy of their marketing activities was the fact that most of them marketed produce on commission basis and less than 1/6th of total produce sold by them was sold as owners. To add to this sorry tale such proportion (i.e. proportion of produce sold as owners), during the decade declined by half from 30% to hardly 15%, Less than half of these societies earned some profit in 1978 while about 31% incurred loss and proportion of profit earning societies also witnessed a decline during the decade. Unfortunately proportion of societies State partnered, of advancing loans, of undertaking marketing, distribution and recovering loans of credit societies also declined

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during the decade. Thus whatever progress, the decade witnessed was confined only to their financial resources and storage activity while their failure was conspicuous in their credit, marketing, distribution and linking of credit with marketing activities. *This leads us to accept hypotheses number 1 and number 2.*

The study of interstate inequality in the performance of PMS in 17 major states of India undertaken with the help of the statistical tools such as the coefficient of variation, the Ginni coefficient of concentration and Lorenz curves indicated that there existed considerable inter state inequality in their performance but fortunately this equality decreased during the decade. *This leads us to accept hypothesis number three.*

Production function analysis was used by fitting the Cobb-Douglas function to the data separately for 1968-69 and 1977-78 to assess the influence of seven variables viz. (i) Short Term Credit, (ii) Medium Term Credit, (iii) Long Term Credit, (iv) Loans advanced by PMS, (v) Value of sales by PMS as owners, (vi) Owned storage capacity of PMS and (vii) Proportion of regulated markets to total markets, on the quantity of agricultural produce sold by PMS in the major 17 states. The results of functional analysis indicate that in 1968-69 all the variables significantly influenced the quantity of agricultural produce sold by PMS but two variables namely Medium Term loans and owned storage capacity exhibited negative influence. This may be explained by the possibility of greater misuse of Medium Term loans as well as that of owned storage capacity (by the private trader members) or by the under-utilised capacity of the owned godowns, which is confirmed by the data analysed in the Chapter on PMS* (Chapters 4 and 5). The Ep or the bi (with values greater than unity i. e. $Ep > 1$) i.e. the total elasticity of production indicated increasing returns and the value of R^2 i.e. the coefficient of determination which was significant at 1% level indicated that about 94% of the variation in the total produce sold by PMS could be explained by the seven variables included in the study. Among the seven variables the greater influence as indicated by higherbi values was of the variables X_7 (proportion of markets regulated), X_4 (value of sales as owners), and X_6 (loans per member advanced by PMS).**

* Trader members use PMS godowns and increase their sales depriving PMS of sale of produce. Similarly they use M. T. loans for purchasing members produce and selling in profitable markets to wholesalers depriving PMS of the business.

** More loans to members means more produce sold and more regulated markets means less unfair competition from private traders.

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In 1977-78 again the Ep indicated increasing return but the value of R^2 which was significant at 5% level indicated that only 56.30% of the variation in the dependent variable was explained by the seven variables included in the study. Again all the variables were significant at different levels except the two variables viz, X_5 and X_7. Further, the three variables namely, X_2, X_5 and X_7 indicated negative influence possibly for the same reasons explained earlier. Greater influence, in this year, as indicated by the bi values was that of X_1 followed by X_3, X_4 and X_6. Thus looking to the analysis for both the years it could be concluded that X_1 (S. T. loans provided by P. A. Cs.), X_3 (L. T. loans provided by L. D. Bs.), X_4 (value of sales as owners by PMS) and X_6 (loans provided by PMS) significantly and positively influenced the quantity of agricultural produce sold by PMS in the 17 major states. *This leads us to accept hypothesis number four partially only for these four variables out of the seven variables included in the study.* The functional analysis thus indicates that if we have to significantly increase the quantity of agricultural produce sold by PMS then adequate S. T. as well as L. T. credit by PACs. and LDBs. and loans by PMS will have to be provided to the members of PMS and the PMS will have to step up their efforts to increase sales mainly as owners by making outright purchases from the members because this is how they are induced to sell through the PMS.

The relation between the cooperative marketing development in the 17 states and the overall agro-economic development was also studied with the use of the Spearman's rank correlation coefficient between the seven indicators of overall agro-economic development such as :

(i) Income per capita (Rs.),

(ii) Literacy percentage,

(iii) Proportion of Scheduled Castes (S. C.) population to total population,

(iv) Proportion of Scheduled Tribes (S. T.) to total population.

(v) Proportion of gross irrigated area to gross sown area,

(vi) Per hectare consumption of fertilizers (kg. per hectare) and

(vii) Yield level of food grains (quintals per hectare) and ten indicators of cooperative marketing development such as,

(i) Membership per society,

(ii) Working capital per member,

(iii) Loans advanced per member,

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(iv) Loans overdue per member,

(v) Agricultural produce sold per member (as owner and as agent),

(vi) Agricultural requisites sold by PMS per member.

(vii) Consumer goods sold by PMS per member,

(viii) Owned storage capacity of PMS per member,

(ix) Profit earned by PMS per member and

(x) Loss incurred by PMS per member.

The 17 states were ranked according to these two sets of indicators and the correlation coefficient was worked out to be 0.53 and tested to be significant at 5% level. Thus it could be concluded that overall agro-economic development has positive and significant correlation with the cooperative marketing development, thus influencing its performance. *This leads us to accept the hypothesis number five.*

EFFECT OF CYCOCEL, ASCORBIC ACID, GIBBERELLIC ACID, PHENYLMERC RIC ACETATE AND KAOLIN ON GROWTH AND YIELD OF WHEAT (VAR. KALYAN SONA) UNDER DRYLAND CONDITION

Moti Lal Bhat Sup : *Dr. N. M. Misra*

This research project was undertaken to study the (i) effect of chemicals on growth, (ii) physiological characteristics,(iii) yield and (iv) uptake of nitrogen, phosphorus and potassium under dryland (barani) conditions. To envisage it, the following two field trials were conducted for two consecutive years at the research farm, Institute of Agricultural Sciences, Banaras Hindu University, Varanasi during rabi 1981-82 and 1982-83.

The soil type of the experimental field was sandy clay loam in texture with pH of 7.6, containing 0.046% total N; 21 kg h^{-1} available P_2O_5; 204 kg h^{-1} available K_2O and 0.404% organic carbon.

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The total precipitation received during crop season was 102.2 mm and 59.5 mm during 1981-82 and 1982-83 respectively. The maximum and minimum temperature ranged from 20.3 to 28.7°C and 7.9 to 14.2°C in 1981-82 and 17.4 to 30.0°C and 7.1 to 17.2°C in 1982-83 respectively. The lowest temperature was recorded in December during 1981-82 and in January during 1982-83.

Field Trial No. 1

"Effect of Cycocel, Ascorbic acid and Gibberellic acid as Seed Treatment on Growth and Yield of Wheat under Dryland Condition". This trial consisted of three chemicals with three levels each viz., (i) cycocel 500 ppm, 1000 ppm and 1500 ppm, (ii) ascorbic acid 50 ppm, 100 ppm and 150 ppm and (iii) gibberellic acid 50 ppm, 100 ppm and 150 ppm in addition to water treatment and no treatment (control), making 11 treatments. The trial was laid out in randomized block design with four replications. The gross and net plot size were 4.50×3.25 m^2 and 4.0×2.25 m^2 respectively. A basal application of 60 kg N, 40 kg P_2O_5 and 30 kg K_2O h^{-1} was applied in the form of urea (46% N); single superphosphate (16% P_2O_5) and muriate of potash (60 kg K_2O) respectively and 5% BHC @ 25 kg h^{-1} was applied to the soil by broadcasting at the final round of working in order to keep the field free from termite infection. The seed was sown @ 100 kg h^{-1} in rows, 25 cm apart on 11th Nov., 1981 and 8th November, 1982. The seed treatment was done as per method—500 g seeds were soaked in 300 ml of prepared solution, i. e., 60% of the weight. This was kept moist for 12 hours and then air dried under shade till the seeds regained their original weight.

Field Trial No. 2

'Effect of cycocel, phenylmercuric acetate, kaolin and ascorbic acid as foliar spray on growth and yield of wheat under dryland condition.' This trial was also laid out at research farm Institute of Agriculture Sciences, Banaras Hindu University, Varanasi in the rabi seasons of 1981-82 and 1982-83. This included control, water spray, one level each of cycocel (1000 ppm); phenylmercuric acetate (100 ppm); kaolin (6 %); ascorbic acid (100 ppm) and two times of application of each chemical viz., full foliar spray at (i) 38th day and (ii) at 68th day after sowing, making 11 treatments and was laid out in randomized block design replicated four times, The gross and net plot size was similar to field trial no. 1. A uniform dose of 60 kg N, 40 kg P_2O_5 and 30 kg K_2O per hectare was applied as basal dressing in the form of urea, single superphosphate and muriate of potash. Wheat variety Kalyan Sona was sown @ 100 kg h^{-1} in rows 25 cm apart on 11th November, 1981 and 8th November, 1982.

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Quantity of chemicals with their respective concentrations per plot was calculated on the basis of 800 litres of water per hectare. 2 CC of 95% ethanol was added for dissolving the requisite quantity of PMA before adding distilled water. Tween 20 was added as wetting agent. Kaolin was stirred while spraying and 1 CC Teepal was added as a sticking agent before spraying.

From the foregoing two field trials, the following results are summarized :

Effect of Cycocel

Cycocel seed treatment significantly reduced the plant height and its effect was greater under CCC @ 1500 ppm than rest of its concentrations. Cycocel @ 1500 ppm produced highest shoot dry weight, This was due to greater number of tillers per plant. Further, cycocel seed treatment @ 1500 ppm exhibited distinct drought tolerance capacity in wheat plants as indicated by higher relative turgidity and leaf moisture which was due to reduced transpiration rate and stomatal frequency. Thus, cycocel seed treatment with 1500 ppm used the soil moisture more economically. This also enhanced the number of ears per hectare (effective tillers) and also reduced the mortality of effective tillers than rest of the cycocel concentrations. On an average cycocel @ 1500 ppm produced highest grain yield of 27.01 q h^{-1} against 19.90 q h^{-1} in control and this increase in grain yield was to the tune of 35.72% over eontrol. This highest grain yield was due to an increase in number of tillers per plant, ear length, fertile spikelets per ear and per spikelet associated with increased test weight. Highest concentration of cycocel i. e., under 1500 ppm enhanced the protein % in grain, uptake of nitrogen, phosphorus and potash (kg h^{-1}) than rest of its concentrations. This was mainly due to highest grain yield and highest percentage of nitrogen, phosphorus and potassium in grain and straw.

Foliar application of cycocel @ 1000 ppm recorded highest dry matter production when sprayed at 38th day than when sprayed at 68th day. This was due to greater number of tillers per plant. Further, cycocel foliar spray at 38th day recorded enhanced growth, physiological and yield attributing characteristics. This also enhanced the average grain yield (26.02 q h^{-1}) against control (19.62 q h^{-1}) and the increased percentage in grain yield was to the tune of 32.61 whereas, cycocel spray at 68th day enhanced only 17.63 percent grain yield against control. The effect of foliar spray of cycocel was greater at 38th day than its spray at 68th day.

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Effect of Ascorbic Acid

Seed treatment with ascorbic acid @ 150 ppm exhibited greater effect than 100 ppm and 50 ppm concentration. Ascorbic acid @ 150 ppm increased the plant height, tillers number and leaf number per plant which was associated with increased photosynthetic area and thereby enhanced the dry matter production. Ascorbic acid @ 150 ppm used available soil moisture more economically as indicated by increased leaf moisture which was due to reduced transpiration rate and stomatal frequency. Further, ascorbic acid seed treatment with 150 ppm enhanced the average grain yield by 23.51% as against control. This was due to an increase in the number of effective tillers and ear length associated with increased number of fertile spikelets per ear and grains per ear. Ascorbic acid seed treatment also enhanced the protein per cent in grain and uptake of nitrogen phosphorus and potassium, which was mainly due to increased grain and straw yields.

Foliar spray of ascorbic acid @ 100 ppm at 38th day enhanced the growth, physiological and yield attributes than its spray at 58th day. This also enhanced the average grain yield (23.81 q h^{-1}) as against control (19.62 q h^{-1}) and this increase was to the tune of 21.35%.

Effect of Gibberellic Acid

Seed treatment with gibberllic acid @ 150 ppm exerted greater effect than GA_3 seed treatment with 100 ppm and 50 ppm. GA_3 @ 150 ppm increased the dry matter production which was due to an increase in tiller number per plant and number of green leaves associated with greater photosynthetic area. Further, GA_3 @ 150 ppm increased the leaf moisture and relative turgidity which was due to reduced transpiration rate and stomatal frequency. GA_3 seed treatment @ 150 ppm enhanced the number of ears h^{-1} and also increased the ear length than rest of the GA_3 concentrations. Highest concentration of GA_3 i.e., 150 ppm recorded greater grain yield (25.22 q h^{-1}) which was 26.73 per cent more than control. This was due to increased number of fertile spikelets per ear associated with more number of grains per ear and test weight. Further, GA_3 seed treatment @ 150 ppm showed higher protein % in grain and uptake of nitrogen phosphorus and potash than the rest of its concentrations and control.

Among chemical seed treatments, greater effect on growth, physiological yield attributes, grain and straw yields, grain quality and uptake of nitrogen, phosphorus and potash was under higher concentrations than lower concentrations. Greater effect was with cycocel @ 1500 ppm followed by GA_3 @ 150 ppm and AA @ 150 ppm.

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Effect of Phenylmercuric Acetate (PMA)

Foliar spray of PMA at 38th day exerted its greater effect than PMA spray at 68th day. Foliar spray of PMA at 38th day increased the dry matter production which was due to an increase in number of tillers, number of leaves associated with increased photosynthetic area. PMA spray at 38th and 68th day increased the leaf moisture and relative turgidity than control which was due to reduced stomatal frequency which ultimately led to reduction in transpiration rate. PMA spray at 38th day significantly enhanced the number of ears per hectare and ear length. This was associated with greater number of fertile spikelets and number of grains per ear.

This increase in yield attributes increased the grain and straw yield than PMA spray at 68th day. The average grain yield was increased by 18.60 per cent over control. PMA spray significantly increased the protein per cent in grain which was due to an increase in nitrogen per cent in grain and straw.

Effect of Kaolin

Among the two antitranspirants i.e.. PMA and kaolin, kaolin spray at 38th day exhibited its greater effect. Kaolin (6%) spray at 38th day increased the number of tillers per plant, number of leaves and photosynthetic area which ultimately led to greater dry matter production. Kaolin spray increased the leaf moisture and relative turgidity due to reduction in transpiration rate which inturn was mainly due to reflectivity of incidental rays. Thus, the moisture available was used more efficiently by the plants. Kaolin spray at 38th day increased the average grain yield by 22.62% over control which was due to increased number of ears h^{-1}, ear length associated with greater number of fertile spikelets and number of grains per ear. Kaolin spray at 38th day also increased the protein % in grain which was due to increased nitrogen % in grain.

The chemicals viz., CCC, PMA, Kaolin and AA applied as foliar spray, did not show its effect on phosphorus and potash uptake.

Foliar spray of CCC, PMA, kaolin and AA exhibited its greater effect at 38th day than 68th day spray and this greater effect on growth, yield attributes and grain straw yields was with cycocel @ 1000 ppm followed by kaolin @ 6%.

Chemicals used as seed treatment and foliar spray, did not show any effect on test weight during first year. Whereas test weight increased in second year. This indicates that the effect of chemicals is not apparent when sufficient moisture is available, while the effect of chemicals is more under droughty conditions.

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Conclusion

From the foregoing results of the two field trials, the following conclusion may be drawn.

1. Pre-sowing seed treatment of lower concentrations does not have beneficial effect on grain yield under dryland condition,
2. Seed treatment with cycocel @ 1500 ppm was superior to rest of the treatments both in enhancing the grain yields and from the economic point of view,
3. Seed treatment with higher concentration of cycocel (1500 ppm) may be used as safeguard against unpredictable weather conditions, especially when wheat is grown under dryland (rainfed) conditions,
4. Foliar application of chemicals should be done at early stage of crop growth (38th day after sowing) and not at late crop growth stage (68th day),
5. Among the two antitranspirants, kaolin proved to be the best in comparison to phenylmercuric acetate,
6. Although, foliar spray of cycocel increased the grain yield as compared to kaolin spray but from the economics point of view kaolin foliar spray is superior.

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AGRONOMY

INDUCING DROUGHT TOLERANCE IN BARLEY (HORDEUM VULGARE L.) VARIETIES WITH POTASH APPLICATION UNDER BARANI (RAINFED) CONDITION

Aluri Jagannatham Sup : *Dr. N. M. Misra*

This research project was undertaken to study (i) the adaptability of barley varieties under barani condition; (ii) to induce drought tolerance in barley varieties through pre-sowing seed treatment with potash and methods of potash application; (iii) to evaluate the suitable concentration of potash for seed treatment, (iv) to assess the uptake of nitrogen, phosphorus and potassium and protein per cent of grain at maturity and (v) to find out the relationship between potassium and proline on drought tolerance in barley varieties under barani condition. To envisage it, the following two field trials were conducted for two consecutive years at the research farm, Institute of Agricultural Sciences, Banaras Hindu University, Varanasi, during rabi seasons of 1977-78 and 1978-79.

The soil of the experimental field was sandy clay loam in texture with pH of 7.5 containing 0.041% total nitrogen; 19.9 kg h^{-1} available P_2O_5, 173 kg h^{-1} available K_2O and 0.345% organic carbon.

The total precipitation received during the crop season was 146.9 mm and 88.1 mm during 1977-78 and 1978-79 respectively. The maximum and minimum temperature ranged from 18.5° to 28.3° C and 6.3° C to 20.3° C in 1977-78 and from 19.3 to 30.8° C and 6.9 to 16.6° C in 1978-79 respectively. The lowest temperature (6.3 and 6.9° C) was recorded in February during 1977-78 and in December during 1978-79 respectively.

Field Trial No. 1

"Effect of pre-sowing seed treatment with potash on barley varieties under barani (rainfed) condition". This trial consisted of three barley varieties (V_1-Ratna, V_2-K 12 and V_3-DL 3) in main plots with ten different potash seed treatments viz., control, water treatment, K-0.5%, K-1%, K-1.5%, K-2%, K-2.5%, K-3.5% and K-4% in subplots. The trial was laid out in split plot design replicated thrice. The gross and net plot size were 4×3.6 m^2 and 3.0×2.7 m^2 respectively. A basal dose of 60 kg N, 40 kg P_2O_5 and 30 kg K_2O h^{-1} was applied in the form of urea (46% N), single super phosphate (16% P_2O_5) and muriate of potash (60% K_2O).

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In order to keep the field free from termite infestation, 5% BHC was applied @ 25 kg h^{-1} to the soil at the final round of working with the cultivator. The seed was sown @ 100 kg h^{-1} in rows at 22.5 cm apart on 4th Nov., during both the years. The seed treatment was done as per method—500 g seeds were soaked in 300 ml of prepared potash solution i. e., 60 % of the seed weight. This was kept moist for 12 hours and then air dried under shade till the seeds regained their original weight. The same procedure was adopted for distilled water treatment also.

Field Trial No. 2

"Effect of methods of potash application on barley varieties under barani condition". It consisted of the same three barley varieties as in Field Trial No. 1 and eleven treatment combinations of methods of potash application viz., control (NOK_2O), water spray, full basal (30 kg K_2O h^{-1}), ⅓ basal + ⅔ soil at tillering (t), 2/3 basal + 1/3 soil (t), 1/3 basal + 2/3 soil (t), ½ basal + ½ foliar (t), 2/3 basal + 1/3 foliar (t), 1/3 basal + 2/3 foliar (t), 1/3 basal + 2/3 foliar at tillering and jointing and full foliar at tillering, jointing and flowering stages. This trial was also laid out in split-plot design, replicated thrice. The gross and net plot size were the same as in Field Trial No. 1. A uniform dose of 60 kg N, 40 kg P_2O_5 h^{-1} in the form of urea (46% N) and single superphosphate (16% P_2O_5) was applied behind the plough in furrows just prior to sowing. Potash @ 30 kg h^{-1} was applied in the form of muriate of potash (60% K_2O) as per treatments. Sowing was done on 12th Nov., during both the years.

The requisite quantity of potash per plot was dissolved as per treatments in ordinary tap water and was sprayed @ 1000 litres per hectare. Teepol @ 0.1 percent was added to the solution as a sticking agent. Equal quantity of water used for water spray treatment.

Varietal Differences

The three varieties differed in plant height, tiller number per plant, LAI, and dry matter production; Ratna produced greater plant height, tiller number per plant, LAI and dry weight of all plant parts (leaf, leaf sheath, stem and earhead) and also total dry matter of plant than DL 3 and K 12. The higher total dry matter per plant in Ratna was due to the greater tiller number per plant and dry weight of all plant parts. Further, Ratna exhibited distinct drought tolerance capacity as indicated by higher relative water content, more proline accumulation, low chlorophyll stability index. Ratna produced higher grain yield of 25.95 q h^{-1} than DL 3 (25.11 q h^{-1}) and K 12 (23.69 q h^{-1}). The increased grain yield in Ratna was due to an increase in ear length, grain number per ear, grain weight per ear, test weight of grain and ear number per metre row length. Further, Ratna also

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produced higher straw yield which was due to greater number of tillers per plant, plant height and total dry matter production.

Ratna recorded higher uptake of nitrogen, phosphorus and potassium in plant at various stages of growth and also in grain at maturity. This was mainly due to higher dry matter production, higher percentage of nitrogen, phosphorus and potassium in different plant parts (leaf, stem and earhead) and also due to higher grain and straw yields. Higher protein percent of grain in Ratna was due to greater uptake of nitrogen and its higher percentage in grain. Moisture use efficiency was also higher in Ratna than DL 3 and K 12 due to its] drought tolerance capacity under barani condition.

Effect of pre-sowing seed treatment with potash

Seed treatment with 2.5% potash greatly enhanced growth attributes viz., plant height, tiller number per plant, LAI and total plant dry matter accumulation than rest of the treatments. Further, potash seed treatment @ 2.5% exhibited distinct drought tolerance capacity in barley plants as indicated by higher relative water content, proline accumulation and low chlorophyll stability index. This also enhanced the yield attributes viz., ear length, grain number per ear, grain weight per ear, ear number per metre row length and test weight of grain and thereby enhanced the grain and straw yields.

On an average, seed treatment with 2.5% potash produced highest grain yield of 27.27 q h^{-1} against control [23.33 q h^{-1}) and this increase in grain yield was to the tune of 16.89%. The increase in straw yield under 2.5% potash seed treatment was due to increased plant height, tiller number per plant and total dry matter accumulation. Higher uptake of nitrogen, phosphorus and potassium was noticed in plant at different stages of growth and also in grain at maturity with 2.5% potash seed treatment than rest of the seed treatments and control. This was mainly due to higher percentage of nitrogen, phosphorus and potassium in plant parts and in grain and also due to higher grain and straw yields. Higher protein % of grain under 2.5% potash seed treatment was due to higher nitrogen content in grain. Seed treatment with 2.5% potash enhanced the moisture use efficiency than other seed treatments and control due to more drought tolerance capacity under barani conditions.

Effect of methods of potash application

Application of 30 kg K_2O h^{-1} as half basal + half foliar at tillering stage exerted its greater effect and enhanced the plant height, tiller number per plant. LAI and total plant dry matter than other methods of application water spray and control. Higher relative water content, proline accumula-

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tion and lower chlorophyll stability index were also noticed with half basal + half foliar application of potash at tillering stage. Further, split application of potash as half basal + half foliar at tillering stage enhanced the average grain yield by 23.29 per cent over control. This was due to an increase in the number of ears per metre row length, ear length, grain number and grain weight per ear and also test weight of grain.

Application of potash as half basal + half foliar at tillering stage also enhanced the total uptake of nitrogen, phosphorus and potassium in plant and in grain at maturity. This was due to increased dry matter production, grain and straw yields and also due to higher per cent of nitrogen, phosphorus and potassium in grain and straw.

Further, an increase in protein percentage of grain under this treatment was due to its higher content of nitrogen in grain. Higher moisture use efficiency was found under this treatment which might be due to variation in drought tolerance capacity with deeper and proliferate root system.

Conclusions

From the foregoing results of these two field trials, it is concluded that :

1. Out of the three barley varieties Ratna gave the highest yield and proved to be better suited under barani condition than DL 3 and K 12.
2. Pre-sowing seed treatment with 2.5% potash was found to be superior to rest of the seed treatments in enhancing the grain yield and this method has been found to be cheaper and more economical.
3. Split application of 30 kg h^{-1} potash may also be advocated for achieving higher barley yields under rainfed condition especially when it is applied as half basal + half foliar at tillering stage.

EFFECT OF NITROGEN LEVELS AND HERBICIDES ON GROWTH YIELD AND QUALITY OF JAPANESE MINT *(MENTHA ARVENSIS L.)*

Aparbal Singh Sup : *Prof. M. Singh*

Japanese mint is one of the important essential oil bearing plant. It was introduced in India in the year 1954 from Japan. After preliminary trials on cultivation and production, it was introduced for large scale cultivation in Tarai region of Uttar Pradesh and Punjab where it could find a suitable place in existing crop rotation.

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Being foliage rich crop, Japanese mint responds well to nitrogen application and needs liberal nitrogen fertilization.

The crop is invaded with large number of weed species which causes 60-70% reduction in yield. After the onset of monsoon the situation becomes more alarming when the removal of weeds through conventional methods, becomes more difficult.

The full benefit of nitrogen fertilization can only be derived when weed growth is checked to a bare minimum. The studies made in rice and wheat in relation to nitrogen fertilization and herbicide usage have also indicated considerable nitrogen economy through weed control.

Keeping the above facts in view, the present investigation was planned and carried out at the Agricultural Research Farm, Department of Agronomy, Institute of Agricultural Sciences, Banaras Hindu University Varanasi, during 1979 and 1980 to collect some of the information related to nitrogen fertilization and herbicide usage.

The experiment was laid out in split plot design, keeping the nitrogen levels (0, 60, 120 and 180 kg N/ha) in main plots and herbicides (terbacil, diuron and chloramben each at 1 and 2kg a.i./ha in addition to weedy check and weed free check) in sub-plots. The treatments were replicated thrice. The soil of experimental plot was sandy clay loam in texture, poor in organic carbon and nitrogen and medium in available phosphorus and potassium.

Observations on weed population, dry matter accumulation and nutrients (N, P and K) depletion were recorded. Observations on crop related to sprouting of suckers, height of plant, leaf area index, dry matter accumulation, nutrients (N, P and K) up take, fresh herb and oil yield as well as oil content in fresh herb and menthol content in mint oil were recorded.

Population of grassy as well as broad leaved weeds were significantly influenced by nitrogen application. The maximum weed population was associated with the highest dose (180 kg N/ha) of nitrogen.

Application of herbicides brought down the weed population significantly over unweeded control. Among the herbicides, terbacil applied at 2 kg a. i./ha was the most effective in suppressing the population of both the categories of weeds (grassy and broad leaved) followed by same herbicide at lower dose and diuron 2 kg a. i./ha. Chloramben was the least effective in controlling grassy as well as broad leaved weeds. Diuron controlled dicots most effectively than monocots.

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There was a consistent increase in dry matter of weeds due to the application of nitrogen. A significant difference was observed with each level of nitrogen and the plots fertilized with 180 kg N/ha gave the maximum dry matter accumulation by weeds, The lowest was obtained in the control at all the stages during both the years.

Application of herbicides had distinct effect on weed population and its dry matter over the control (weedy check). Terbacil at higher as well as lower dose was the most effective in suppressing dry matter accumulation whereas, chloramben at 1 kg a. i,/ha proved to be the least effective in this respect. In general, the variation in weed dry matter due to various weed control treatments was of the order of weedy check> Chloramben 1 kg> Chloramben 2 kg> diuron 1 kg> diuron 2 kg> terbacil 1 kg> terbacil 2 kg. Application of higher levels of nitrogen (120 and 180 kg N/ha) to unweeded control and chloramben (1 and 2 kg a. i./ha) treated plots induced remarkable influence on weed dry matter production. The depletion of nutrients (N, P and K) was remarkably effected by nitrogen levels weed control treatments. The depletion of these nutrients increased with increasing levels of nitrogen. The minimum N, P and K depletion was observed in terbacil treated plots whereas, the maximum in chloramben treated plots.

Sprouting of mentha suckers observed 30 and 45 days after planting remained unaffected due to the application of nitrogen. It was only the herbicide which could alter the sprouting significantly. Terbacil stimulated the sprouting significantly over remaining weed control treatments whereas, diuron at 2 kg a. i./ha decreased the sprouting appreciably due to the phytotoxic effect on Japanese mint. Weedy or weed free conditions did not have any impact on sprouting of suckers.

Application of different levels of nitrogen had favourable effect on plant height, leaf area index, leaf shoot ratio and dry matter accumulation by Japanese mint. Application of 180 kg N/ha significantly increased the leaf area index and leaf shoot ratio over lower levels (60 and 120 kg N/ha) and the control. However, the plant height could not be influenced significantly with increase in nitrogen level beyond 120 kg N/ha. There was almost a linear increase in dry matter accumulation with increasing levels of nitrogen. The maximum and the minimum dry matter production recorded with the application of 180 kg N/ha and the control, respectively at all the stages during both the years.

The growth of Japanese mint with regards to plant height and leaf area index, and also the leaf shoot ratio and dry matter accumulalion was positively affected by the weed control measures over unweeded control. Weed free check followed by terbacil 2 kg a. i./ha improved the growth and

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dry matter accumulation of Japanese mint significantly over the remaining herbicidal treatments and the control (weedy check). Diuron at 2 kg a. i./ha was the least effective in stimulating growth and dry matter accumulation of Japanese mint and produced less dry matter than the weedy check.

Weed free check and terbacil 2 kg a.i./ha in combination with higher nitrogen levels were more conducive in increasing dry matter accumulation in Japanese mint.

Removal of N, P and K by Japanese mint increased with increasing levels of nitrogen. The highest nitrogen removal noted at 180 kg N/ha level. However, in case of P and K, increase in nutrient removal could be noticed upto 120 kg N/ha only. Plants grown under weed free conditions removed the maximum nutrients (N, P and K). Among the herbicidal treatments, the maximum removal was noted from the plots where terbacil 2 kg a.i./ha was applied. Diuron applied at 2 kg a.i./ha decreased the nutrients removal significantly over the remaining herbicides and the control.

Profound effect of nitrogen application was observed in respect of fresh herb yield and oil production in Japanese mint. The highest fresh herb and oil yield were associated with the highest dose of nitrogen application (180 kg/ha). The herb and oil yields were the lowest where no nitrogen was applied. The fresh herb yield and oil production in Japanese mint were greatly enhanced with the use of weed control measures. Unchecked weed growth caused a pproximately 75 per cent reduction in yield. Repeated mannual weeding gave the maximum herb and oil yield and was significantly superior to the rest of the treatments. Terbacil 2 kg a.i./ha was next in order of superiority and was statistically superior to the remaining herbicides and the control.

Application of higher doses of nitrogen was more beneficial to weed free check and terbacil (2 kg a.i./ha) treated plots and each increment in nitrogen dose significantly increased the herb and oil yield over lower level. However, such increases were not visible with other treatments. Contrary to the above, yields were decreased with diuron 2 kg a.i./ha when fertilized with 180 kg N/ha rate.

Keeping the field weed free through out the crop growing season and fertilizing with 180 kg N/ha gave the maximum net return per hectare. Terbacil at 2 kg a.i./ha with the same level of nitrogen closely followed the net return obtained with that of weed free check.

Oil content in fresh herb and menthol content in mint oil did not vary due to either of the factors (nitrogen levels and herbicides) under study.

The residual effect of nitrogen levels and herbicides was not evident on the succeeding mustard crop.

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NITROGEN EFFICIENCY IN UPLAND RICE

Jitendra Pratap Singh Sup : *Dr. Kalyan Singh*

Rice (*Oryza sativa L.*), a staple food of more than 60% of the world's total population, is grown in an area of more than 144.9 m.ha (FAI, 1983). In fact 90% of this area under rice is situated in the tropical south and south east Asia. In India it is the most important and extensively grown food crop in the traditional rice belt as well as the non-traditi onal areas of West Bengal, Bihar, eastern and western Uttar Pradesh and Central U. P. to the entire north western region extending upto Himachal Pradesh occupying about 40 m. ha with an average production of 57 m. tonnes (FAI, 1982-83). However, the average yield of the crop is relatively poor. Therefore, in view of the importance of this crop, an increase in total production of rice per unit area and per unit of input is of immediate economic relevance. Among the various inputs of production, fertilizer management specially fertilizer nitrogen is most inportant.

Among the major mineral essential elements, nitrogen continues to be the magic element of agricultural abundance. The potential of nitrogen by rice in the country towards establishing mean rice yield at 2.4 tonnes/ha, assuming that the percentage irrigated area will rise to 50% and coverage under high yielding varieties will be around 42%, is estimated to be 65 kg N/ha as against the current level of nitrogen consumption of 25 kg N/ha (Stangel, 1979). This lag between the actual and potential could be explained in large part by the varying abilities of the farmers to accept the risk involved in fertilizer use under uncontrolled, erratic water situation and more complex system of rice farming in the country. The environmental barriers and soil conditions adding to the risk factor is further compounded by the lack of an appropriate technology for fertilizer use under such erratic and adverse conditions. The low nitrogen recovery of rice (11 to 50%) particularly when applied at early stages of crop growth (De Dutta *et al.*, 1969 and Prasad *et al.*, 1970, I. A. R. I., 1980 and Singh and Singh, 1980) is a major deterrent to the use of required quantity of fertilizer nitrogen by the modorn rice varieties.

Keeping these facts in view the present investigation "Nitrogen use efficiency in upland rice" was carried out at the Agriculture Research Farm, Department of Agronomy, Varanasi, during 1982-83 and 1983-84 with a view to gather information regarding relative efficiency of some slow-release nitrogenous fertilizers. The soil of the experimental field was sandy loam in texture having pH value of 7.1, low in nitrogen and organic carbon contents and medium in available phosphorus as well as

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potasstum. The combination of seven main plot treatments of nitrogen sources (urea split, sulphur coated urea, neem coated urea. lac coated urea, gypsum coated urea, urea super granules and urea, coal acid) and four sub-plot treatments of nitrogen levels (0 kg, 40 kg, 80 kg and 120 kg) were laid out in split plot design and was replicated thrice. Amongst the different nitrogen sources, sulphur coated urea, neem coated urea, lac coated urea, gypsum coated urea, urea super granules and urea coal acid were used as slow release nitrogenous fertilizers and straight urea (urea split) was used as a check. The full doses of all the coated fertilizers were applied after one week of transplanting. In case of urea best split (straight urea), half of the amount of nitrogen was applied at transplanting and remaining amount was applied in two equal splits at tillering and panicle initiation stages of crop growth. The whole amount of phosphorus and potash each at the rate of 50 kg/ha was applied as broadcast through single super phosphate and muriate of potash, respectively in all the plots before transplanting. The succeeding crop of wheat was taken as a residual crop and uniform dose of 50 percent of recommended nitrogen (60 kg N/ha) and full doses of phosphorus (60 kg $P_2 0_5$/ha) and potassium (60 kg $K_2 0$/ha) were given to all the treatments including urea split taken as a check at seeding time using urea, single super phosphate and muriate of potash as source of fertilizers.

Nitrogen Sources

The experimental findings clearly revealed that nitrogen sources differed significantly among themselves during the two years of investigations with respect to different growth characters.

Among the different sources tried, urea super granules had tallest plant at all the stages of crop growth and smallest plant were observed under urea coal acid.

Similarly, urea super granules produced the highest number of tillers at all the stages during both the years while urea coal acid had the lowest number of tillers/hill.

Urea super granules also assimilated the highest amount of dry matter during both the years at all the stages but it was significantly superior to only urea coal acid which had the lowest amount of dry matter.

In general, among the different sources tried, sulphur coated urea was found to be the next best treatment after urea super granules with respect to plant height, number of tillers/hill and dry matter accumulation/hill.

The different nitrogen sources did not differ significantly during two years of investigation with respect to number of filled and unfilled grains per panicle. However, higher value for filled grains/panicle was observed

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with urea super granules while the lower one was recorded under urea coal acid and urea split.

Contrary to this, the number of unfilled grains were higher under urea coal acid and urea split.

Nitrogen sources also varied significantly with respect to panicle length only during the first year and all the sources were significantly superior to urea coal acid during the first year. In general, the maximum panicle length was associated with urea super granules during both the years of experimentation.

The different nitrogen sources also varied significantly with respect to thousand grain weight during two years of investigation and urea super granules had significantly higher thousand grain weight as compared to other nitrogen carriers during both the years except sulphur coated urea which was at par with urea super granules during the second year.

Grain yield was also affected due to different slow-release nitrogenous fertilizers and urea super granules produced the highest grain yield followed by sulphur coated urea and neem coated urea while the lowest grain yield was recorded under urea coal acid during both the years. In pooled analysis also urea super granules produced the highest grain yield (q/ha) but it was at par with the next best treatment (q/ha) but it was at par with the next best treatment (sulphur coated urea). Neem coated urea also significantly increased the grain yield over urea coal acid.

Straw yield was significantly affected due to different nitrogen sources and urea super granules produced significantly higher yield (q/ha) as compared to urea coal acid, lac coated urea and over urea split during the first year. However, during the second year it was significantly superior to coal acid, urea split and lac coated urea. The next best treatments with respect to straw yield were sulphur coated urea and neem coated urea.

Among the different quality characters, the highest crude protein content (%) in grain and straw was noticed under urea coal acid during both the years.

Contrary to protein content, the highest protein harvest in grain and straw was associated with sulphur coated urea and urea super granules whereas urea coal acid had the lowest value for protein harvest.

Protein translocation efficiency was, however, again higher under urea coal acid.

The aparent nitrogen recovery (%) was, in general, heighest under urea super granules followed by sulphur coated urea. The lowest apparent nitrogen recovery (%) was however noted in urea split.

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On an average, urea coal acid had the highest amount of actual nitrogen after rice harvest and the lowest value of nitrogen was recorded under sulphur coated urea followed by urea super granules. The net loss of nitrogen was the highest under urea split. The minimum loss of nitrogen was obtained with sulphur coated urea followed by neem coated urea.

The highest residual effect on succeeding wheat crop in respect of grain and straw yield was obtained with urea coal acid followed by lac coated urea and gypsum coated urea whereas the lowest residual effect was noted with urea split.

Nitrogen Levels

The nitrogen levels also varied with respect to growth characters and the values of all the growth characters increased with increasing levels of fertilizer from 0 kg to 120 kg N/ha.

Nitrogen levels also varied with respect to yield and yield attributes and the values of the yield attributes namely, number of filled grains/panicle panicle length and thousand grain weight increased with increasing levels of nitrogen showing the highest value under the highest level of N. However, number of unfilled grains were highest under controlplots.

The grain and straw yields also increased significantly with increasing levels of nitrogen and the highest grain and straw yields were recorded with 120 kg N/ha.

The N, P, K contents at different stages of crop growth and their uptake at harvest increased with increasing levels of nitrogen during both the years.

The response function fitted to nitrogen levels on mean grain yield of rice showed that the quadratic term was significant and the economic optimum nitrogen dose was 132 kg N/ha.

The net loss of nitrogen in soil increased with increasing levels of nitrogen recording the highest values with the highest level of N.

The highest grain and straw yields of succeeding wheat crop were obtained with highest level of 120 kg N/ha during both the years.

Conclusions :

On the basis of experimental findings, the following conclusions may be drawn :

1. Urea supergranules should preferably be used as a promising nitrogen source at higher level of nitrogen. However, at lower level of nitrogen application, urea coal acid and gypsum coated urea should be preferred.

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2. The apparent nitrogen recovery is higher with urea super granules followed by sulphur coated urea.
3. Urea coal acid left the highest residual effect as compared to other nitrogen sources followed by lac coated urea and gypsum coated urea.

From the aforesaid conclusion, it is hereby inferred that during the present era of energy crisis, escalating prices of petro-chemicals and low nitrogen recovery under complex rice eco-systems, it would be worthwhile to popularise the use of newly evolved promising urea super granules not only for increasing the rice yield but also to stabilise its production by increasing nitrogen use efficiency. The results with sulphur coated urea are also very fascinating but its price may be, at present, prohibitive specially under Indian conditions.

TO STUDY THE POSSIBILITY OF USING FLY ASH IN COMBINATION WITH NPK ON GROWTH AND YIELD ATTRIBUTES OF RICE AND WHEAT

Nagendra Bahadur Singh Sup. *Dr. Mahatim Singh*

A vast quantity of coal is being burnt in the thermal power plants for the purpose of power generation. The utilisation of coal in power generation results in production of huge quantities of waste product (fly ash). Since the fly ash is partly or wholly a burnt material, it may have some of the properties of coal as well as the burnt ash. It was thought that some ways and means be evolved for its proper utilisation in agriculture.

Apart from the extremely unsatisfactory low levels of fertilizer application major nutrients too are utilised in an unbalanced proportion. Therefore, balanced fertilizer application and good manarement of soil appear to be the possible means of raising the agricultural production. It was intended to work out the effect of fly ash on soil and crop growth as well as the fertilizer needs under field conditions and to assess the performance to varying environmental manipulations and agronomic practices and finally to estimate the crop removal of nutrients and soil fertility changes as a result of fertilizer application under this project entitled "To Study the Possibility of Using Fly Ash in Combination with NPK on Growth and Yield Attributes of Rice and Wheat". The field experiment was conducted at the Research Farm, Department of Agronomy, Banaras Hindu University, during 1980-

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81 and 1981-82. The soil of the experimental field was saline-alkali having pH of 8.0 and EC 0.390 mmhos/cm. The experiment was laid out and conducted in a split plot design with 12 treatments in all which were replicated three times. Treatments consisted of three fertility levels (60 kg N+40 kg P_2O_5+30 kg K_2O, 80 kg N+40 kg P_2O_5+40 kg K_2O and 120 kg N+80 kg P_2O_5+ 60 kg K_2O/ha) and three fly ash percentage, viz., 10, 20 and 30 per cent in addition to one control.

The calculated amount of fly ash was mixed evenly in the soil upto the depth of 30 cm. After the application of fly ash all the plots were kept submerged for a period of about 25 days by supplying 5-7 cm of standing water and after which the rice crop was transplanted during both the years of experimentation. Phosphorus was applied as basal at the time of rice transplanting and wheat sowing, whereas 50 per cent of potassium was applied at the time of rice transplanting and wheat sowing and the remaining 50 per cent of it was top-dressed after 50 days of rice transplanting and wheat sowing. Nitrogen, on the other hand, was applied in 3 split doses, i.e., 50 per cent at the time of rice transplanting and 25 per cent each at 25th and 50th day after rice transplanting and wheat sowing. Urea, single superphosphate and muriate of potash were used as sources of nitrogen, phosphorus and potassium, respectively.

To study the influence and efficiency of fly ash on soil pH and EC were recorded at different stages. A number of growth observations were recorded at 25 days interval during both the years of experimentation. Data on yield and yield components were recorded at post-harvest stage. Plant samples collected at various stages of growth were analysed for nitrogen, phosphorus and potassium contents and their uptake in grain and straw were calculated accordingly. After harvest of the crop the soil samples from respective plots were drawn and analysed for available nitrogen, phosphorus and potassium status. The salient findings are summarized hereunder :

Growth and Growth Analysis

The mean height of plant, in general, showed superiority of plants grown under the high fertility level over those under the medium and low fertility levels at all the growth stages of the crop during both the years o experimentation. Application of fly ash failed to produce significant influence on plant height at early growth stages. However, fly ash application enhanced the plant height significantly at later growth stages over the control.

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Number of tillers were significantly influenced by fertility levels at all the growth stages of the crop. The maximum number of tillers were obtained at 75 days after transplanting and thereafter a decrease in total tillers were observed. A consistent increase in total number of tillers/hill were recorded with increase in percentage of fly ash from 10 to 20 per cent over the control, but further increase in fly ash to the tune of 30 per cent decreased the total tillers/hill during both the years, respectively.

Fertility levels had positive effect on the dry matter production from 25 days after transplanting to maturity. The high fertility level produced significantly more dry matter accumulation over the medium as well as low fertility level at all the growth stages. Fly ash had no significant effect on dry matter production during 1980, whereas during 1981 fly ash increased dry matter production significantly at all the sampling dates. Application of fly ash to the tune of 20 per cent increased the dry matter production significantly over the control and 10 per cent fly ash application.

Maturity Characters

With an increase in fertility level all the yield components such as productive tillers per hill, panicle length, total number of grains/panicle, grains filled/panicle and 1000 grain weight significantly increased, but the differences in the number of unfilled grains per panicle was not singificant due to fertility levels. In the second year, there was a general reduction of yield attributes except the test weight in comparison to the first year.

With an increase in fly ash levels upto 20 per cent, all the yield attributes, such as productive tillers/hill, panicle length, total number of grains/panicle, grains filled/panicle and 1000 grain weight, progressively increased over the control and 10 per cent fly ash during both the years, However, during 1981 fly ash application could not reach to the level of significance in increasing the grains filled per panicle. Applications of fly ash to the tune of 30 per cent decreased the yield attributes over the 20 per cent fly ash application, but on the contrary 30 per cent fly ash increased these characters over the control and 10 per cent fly ash during both the years of experimentation.

Yield

The maximum grain yield (47.14, 46.62 q/ha) and straw yield (52.67, 50.45 q/ha) was obtained under the high fertility level which was significantly superior over the medium and low fertility level, but the yield differences due to medium and low fertility level were not significant. However, the yield of grain as well as straw increased consistently with an increase in fertility level during both the years of study.

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The findings revealed that the maximum grain yield was obtained with 20 per cent fly ash which was significantly superior over the control and 10 per cent fly ash application. However, during 1980, application of fly ash to the tune of 30 per cent reduced the grain yield significantly, but remained at par with 20 per cent fly ash application during 1981. A consistent increase in straw yield was recorded with increasing level of fly ash upto 20 per cent fly ash and further increase at the rate of 30 per cent caused significant reduction in straw yield during both the years.

Qualitative

The maximum concentration of N, P and K were recorded with high fertility and the minimum under the low fertility level at all the stages. The percentage of N, P and K was found to be higher in early stages which declined with the advancement in the age of the plants. Application of fly ash to the tune of 20 per cent increased the percentage of N, P and K over the control and 10 per cent fly ash application.

As regards the concentration and uptake of N, P and K in grain and straw it was found that most of the absorbed N and P moved to the grain leaving behind very low concentration in straw while the reverse trend was noted in the case of potassium. The percentage as well as uptake of N, P and K in grain and straw was the maximum under high fertility level and the minimum under the low fertility level.

Percentage as well as uptake of N, P and K was the maximum under the plots with 20 per cent fly ash, but, further increase in percentage of fly ash (30%) decreased the percentage as well as uptake of N, P and K in grain and straw, respectively.

Crude protein percentage was influenced with levels of fertility as well as the fly ash. The maximum protein content was observed under the high fertility level, on the other hand, application of 20 per cent fly ash resulted in the maximum protein content during both the years.

Effect of Fertility Levels and Residual Effects of Fly Ash on Wheat

Growth and Maturity Characters

Plant height and total tillers increased with increase in fertility levels with the maximum values under high fertility level and the minimum under low fertility level. However, during 1981 fertility level would not reach to the level of significance in increasing the total tillers. Residual effect of fly ash was found to be effective in increasing the plant height and total tillers and the values being maximum under the treatments receiving 20 per cent fly ash and the minimum under the control.

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With an increase in fertility level the yield components, such as, effective tillers, length of earhead, number of grains per earhead and 1000 grain weight, increased during both the years and the values being maximum under high fertility and the minimum under the low fertility level. Residual effect of fly ash was found to be operative in increasing the yield components. But such a increase was noted only upto the 20 per cent fly ash and further increase in its rate (30%) decreased these components over the residual effect of 20 per cent fly ash.

Yield

The maximum grain yield (35.56 and 29.71 q/ha) and straw yield (56.73 and 43.03 q/ha) were obtained under high fertility level and the minimum under the low fertility level (26.79, 24.70 and 42.22, 38.67 q/ha). During 1981 high fertility level significantly increased the grain and straw yield over the medium and low fertility level, but during 1982 high fertility level significantly increased only over the low fertility level but remained at par with the medium fertility level.

The maximum grain and straw yields were recorded under the treatment receiving 20 per cent fly ash which significantly increased over the control and 10 per cent fly ash. However, residual effect of 30 per cent fly ash decreased the grain and straw yield over the 20 per cent fly ash, but on the contrary increased over the control and 10 per cent fly ash during both the years of experimentation.

Qualitative

The percentage as well as uptake of N, P and K in grain and straw was maximum under the high fertility level and the minimum under the low fertility level. Residual effect of fly ash to the tune of 20 per cent increased the percentage as well as uptake of N, P and K, but, further increase in its rate decreased the percentage as well as uptake of N, P and K in grain and straw. In general, it was found that most of the absorbed N and P moved to grain leaving behind very low concentration in straw, while the reverse trend was noted in the case of potassium.

Effect of Fertility Levels and Fly Ash on Soil

Findings revealed that there was no significant effect of fertility levels on the soil pH and electrical conductivity.

Application of fly ash was found to be operative in decreasing the pH of soil at all the stages. Fly ash application to the tune of 20 and 30 per cent decreased the soil pH significantly over the control and 10 per cent

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fly ash, but remained at par between themselves. Similarly, application of 10 per cent fly ash decreased the soil pH significantly over the control during both the years at all the stages. Application of 20 and 30 per cent fly ash increased the electrical conductivity over the control and 10 per cent fly ash, and 10 per cent fly ash application over the control at all the stages.

Conclusion

On the basis of the findings of the present investigation the following recommendations of practical utility emerged out :

(1) High fertility level (120+80+60) was the best treatment giving maximum grain and straw yield in both the years.

(2) Applications of 20 per cent fly ash was found suitable for the reclamation of saline-alkali soil.

(3) Fly ash can be used to the tune of 20 per cent only for getting higher grain and straw yield.

PRODUCTION POTENTIAL OF INTENSIVE CROP ROTATIONS UNDER RESOURCE CONSTRAINTS

Radhey Shyam Singh Sup. *Dr. Mahatim Singh*

The world, in general, and developing countries, in particular, are finding it extremely difficult to feed the fast growing population. As such the major problem today appears to be the production of foodgrains. As far as the production of foodgrains in the country is concerned, it is quite low as compared to many other developed countries of the world. However, it is interesting to note that this present levels of production is obtained at a very low level of inputs and technology unlike the near saturation point reached in many developed countries. This raises our hope and gives us an opportunity to produce more by bridging the gap between potential yields and the actual production realised. Therefore, answer to achieve self-sufficiency in foodgrains lies in increasing the yield per unit area per unit time through adoption of improved technological advancement and their agronomical manipulations depending upon ecological-cum-economic need of the regions.

Among the various gradients of new technology, intensive cropping is an important tool of the present day agriculture to increase the productivity of land. It is essentially a programme for irrigated area provided

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with balanced fertilizer use and need based plant protection measures. With these facilities, it is not only possible to increase the cropping intensity but crop yields can be increased and established.

The farmers of eastern Uttar Pradesh, particularly Varanasi region, grow rice in *Kharif* and wheat in *rabi* seasons under intensive cropping programme. Wheat yield in the country has increased tremendously from 8 million tonnes during early sixties to nearly 33 million tonnes at present due to introduction of Mexican wheat varieties and the implementation of advanced technology suited to exploit production potential of the crop. But the continuous use of rice-wheat rotations has shown reduction in total crop yields. It is, therefore, essential that the crops other than wheat like pulses and oilseeds should be grown in *rabi* season after *kharif* rice to establish the crop yield as well as to restore the soil fertility.

However, the success of intensive cropping programme is solely dependent on the availability of resources, particularly fertilizer and irrigation. Production of fertilizer in the country continues to lag behind our requirements. Similar to fertilizer, availability of irrigation water is scarce and uncertain. Therefore, it has become imperative to find out ways and means to exploit the marginal and available resources under resource constraints to maximum agricultural production per unit fertilizer and water used. However, very little systematic efforts have been made on this aspect. Hence, the proposed investigation entitled "Production potential of intensive crop rotations under resource constraints" was taken up.

Field experiments were conducted in split plot design with combination of alternative crops (wheat, bengal gram, mustard) and levels of irrigations (higher and lower levels of irrigation) in main plots and fertility levels (100, 75, 50 and 25% of recommended doses of fertilizers) in sub-plot during *rabi* season of 1977-78 and 1978-79 after base crop of transplanted rice which did not involve any treatment. There were two levels of irrigation for wheat i.e. higher and lower levels. The higher levels of irrigation included application of irrigation water at C.R.I., tillering, jointing, flowering and milk stages whereas lower levels of irrigation included application of irrigation water at C.R.I. and milk stages. In case of bengal gram the higher levels of irrigation indicated application of water at pre-flowering (70 days after seeding)whereas lower level of irrigation was taken as control where no irrigation water was applied. In case of mustard the two irrigation levels, higher and lower represented the application of water at pre-flowering stage (25 days after seeding) and grain formation stages (70 days after seeding) as higher and lower levels of irrigation, respectively.

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The four levels of fertility in case of wheat were 120:60:60, 90:45:45, 60:30:30 and 30:15:15 of N, P_2O_5 and K_2O kg/ha, respectively. In case of bengal gram the four fertility levels were 20:60:30, 15:45:22.5, 10:30:15 and 5:15:7.5 of N, P_2O_5 and K_2O kg/ha, respectively. In case of mustard four fertility levels were 90:60:40, 67.5:45:30, 45:30:20 and 22.5:15:10 of N, P_2O_5 and K_2O kg/ha, respectively. The experimental soil was sandy clay loam having pH 7.4, low in nitrogen and organic carbon contents and medium in availab'e phosphorus and potassium. A uniform dose of 120:60:60 N, P_2O_5 and K_2O kg/ha, respectively was applied to rice during *kharif* season. In case of *rabi* crops the fertilisers were applied as per treatment. Besides grain and straw yield of rice, observations were recorded on growth, yield, yield attributes and quality of produce in wheat, bengal gram and mustard.

The NPK uptake by grain and straw of wheat, bengal gram and mustard were also worked out. The composite sample from 0-30 cm soil layer before seeding were analysed for nitrogen, available phosphorus and potassium. Composite samples were also analysed for some single value physical constants viz. bulk density, field capacity and wilting point. The economics of crop production under different treatment was also worked out.

The application of irrigation water in wheat significantly affected the drymatter production and the application of irrigation water at C.R.I., tillering, jointing and milk stages had significantly higher amount of drymatter assimilation as compared to lower level of irrigation.

The higher level of irrigation was also significantly superior to lower level of irrigation with respect to all the yie'd attributes. The application of irrigation water also had significant effect on grain and straw yields of wheat and the application of irrigation water at five different critical stages namely C.R.I., tillering, jointing, flowering and milk stages produced significantly higher yields as compared to its lower level where irrigation water was applied only C. R. I. and milk stages.

Protein content in grain as well as NPK uptake by grain and straw were also significantly affected by irrigation levels and the highest values of these characters were associated with higher level of irrigation. The consumptive water use was also affected by irrigation levels and higher irrigation levels had the highest value of consumptive water use. The moisture use efficiency, however, was highest under the lower level of irrigation.

In case of Bengal gram also the drymatter assimilation was highest under the higher level of irrigation where irrigation was applied at pre-

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flowering stage. The yield attributes as well as grain and straw yields were also significantly affected by irrigation levels and the values of all the yield attributes were higher when bengal gram was irrigated at pre-flowering stage. These characters together led to higher grain and straw yields under higher level of irrigation. The crude protein content as well as NPK uptake in grain and straw were also affected by irrigation treatments. The highest values of NPK uptake were obtained with higher level of irrigation. The consumptive water use of bengal gram was also affected by irrigation treatments and higher amount of irrigation water had higher value of consumptive use. However, water use efficiency was highest with lower level of irrigation.

In case of mustard also the irrigation levels differed significantly and drymatter accumulation was highest under the higher level of irrigation when irrigation was applied at pre-flowering as well as grain formation stages.

The values of yield and yield attributes were also higher under higher level of irrigation where irrigation water was applied at pre-flowering and grain formation stages as compared to lower level of irrigation where irrigation was applied only at pre-flowering stage.

The oil content as well as NPK uptake were also affected by irrigation treatments and the highest values of these characters were associated with higher number of irrigation.

Consumptive water was also higher under the higher irrigation levels but the highest value of water use efficiency was associated with lower level of irrigation.

Like irrigation treatments fertility treatments also varied significantly in all the crops with respect to almost all the observations. In case of wheat drymatter production per plant increased significantly with increasing levels of fertility and the drymatter accumulation was highest with 120:60:60 N, P_2O_5 and K_2O Kg/ha, respectively.

The yield and yield attributes were also affected by fertility levels and the highest fertility levels had the highest grain and straw yields as well as the highest value of yield components.

The crude protein content in grain as well as NPK uptake by grain and straw were also significantly affected by fertility levels and application of 120 Kg N, 60 Kg P_2O_5, 60 Kg K_2O/ha had significantly higher values of these characters as compared to other fertility treatments.

The consumptive water use as well as water use efficiency were also higher under the higher level of irrigation.

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In case of Bengal gram fertility levels differed significantly among themselves and the highest amount of drymatter was associated with highest level of fertility (20:60:30). The yield and yield components were also significantly affected by fertility levels and the higher level of fertility had higher values of all the yield attributes and also produced highest amount of grain and straw per hectare.

The crude protein content in grain as well as NPK uptake by grain and straw were also significantly affected by fertility levels and values of NPK uptake as well as protein content were highest under the highest level of fertilitp.

The fertility level also affected consumptive use of water, water use efficiency and the highest values of both characters were associated with the highest level of fertility.

When the cropping sequence was taken into consideration taking rice as a base crop during *kharif* and wheat, Bengal gram and mustard during *rabi* seasons, it was observed that the rice-wheat cropping sequence produced the highest amount of grain yield (c/ha) and it was followed by rice-bengal gram and rice-mustard. The rice-wheat cropping sequence produced maximum food grain/ha when wheat during *rabi* season was given 5 irrigations at C.R.I., tillering, jointing, flowering and milk stage and was supplied with 120 Kg N, 60 Kg P_2O_5, 60 Kg K_2O/ha. The net return/ha was, however, highest under the cropping sequence rice-mustard. On the basis of experimental findings, the following conclusion were drawn :

1. Wheat crop should be given 5 irrigations at C.R.I., tillering, jointing, flowering, milk stages to maximise grain yield.
2. Wheat crop should be fertilised with 120:60:60 of N, P_2O_5 and K_2O Kg/ha, respectively to ensure higher and sustained grain yield.
3. Bengal gram should also be irrigated a tpre-flowering (70 days after sowing) to get maximum grain yield/ha.
4. Gram responded favourably to fertility levels and best result could be obtained with application of 20 N, 60 P_2O_5 and 40 K_2O Kg/ha.
5. Mustard crop should also be irrigated at pre-flowering and grain formation stages for maximising grain production.
6. Mustard crop also responded favourably to fertility levels, therefore, for getting higher yield, this crop should also be fertilised with 90:60:40 Kg N, P_2O_5 and K_2O/ha.
7. Among the cropping sequences, rice-wheat cropping sequence produced maximum grain and this followed by rice-gram and rice-mustard.

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8. Economics of cropping sequence clearly indicated rice-mustard as most economical cropping sequence for agro-climatic conditions similar to eastern U. P. The maximum profit for this cropping sequence can only be obtained when mustard was irrigated at pre-flowering and grain formation stages and was supplied with 90 Kg N, 60 Kg P_2O_5 and 60 Kg K_2O/ha under condition when both irrigation water and fertilizer are adequately available.

9. Under resource constraints, where irrigation water is inadequate, the maximum benifiet from this cropping sequence can be obtained by giving one irrigation at pre-flowering stage and by applying 100% recommended dose of 90:60:40 Kg N, P_2O_5, K_2O/ha, respectively.

10. Under the situation where fertilizer availability is inadequate, the maximum benefit can be acrued by applying irrigation at pre-flowering and grain formation stages with 75% recommended dose of N, P_2O_5 and K_2O/ha (67.5:4S:30) to the crop.

STUDIES ON THE EFFICIENCY OF HERBICIDES IN RICE UNDER DIFFERENT WATER MANAGEMENT PRACTICES

Ramesh Kumar Singh Sup. *Dr. R. P. Singh*

Rice is a semi-aquatic plant and enjoys the presence of standing water throughout its growth. Although the practice of continuous submergence is the best for good harvest of rice and weed control. However, maintenance of continuous saturation or intermittent flooding may produce rice yield comparable to continuous submergence, particularly during *Kharif* season when considerable amount of rainfall occurs. Rice is a major consumer of the three scarce commodities, energy, water and fertilizer. The need for energy conservation through good water management practices is urgent especially in view of the increasing energy crises with declining water tables and increasing irrigation acreage.

Flooding is an important practice for weed control. Factors affecting the efficacy of flooding to control weeds are time of flooding, depth of flooding, stage of development of the weed, weedsps. to be controlled and seeding depth of the weeds. Weed emergence is closely related to the moisture content of the soil and the depth of flooding. Flooding induces difference in germination and growth responses in different weed species. Further,

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weed species differed with soil moisture content and depth of flooding. Previous work done on this aspect has revealed that few or no seedling of *Echinochloa crus-galli*, *Brachiaria platyphylla*, *Aeschynomene*, *virginica* and *Sesbania exaltata* emerged when the soil was flooded, but at field capacity or saturation, satisfactory stand of all species developed. The best growth and development of *Echinochloa crus-galli*, *Cyperus iria*, *Cyperus defformis*, *Fimbristylis dichotoma* occured when the soil was saturated.

The efficiency of herbicide has intense relation with soil moisture condition and its effect is markedly reduced under dry condition. Although, some efforts have been made by a number of weed scientists to co-relate the soil moisture conditions with the effectiveness of herbicides. As rice is grown under diversified conditions, and the composition of rice weed communities is strongly influenced by the types of water management and cropping system utilized.

Therefore, the present study entitled "Studies on the efficiency of herbicides in rice under different water management practices" was conducted during two consequitive years, 1982 and 1983 to draw definite relation between water management practices and efficacy of herbicides.

The experiment was conducted in split-plot design, with twenty eight treatment combinations. Water management practices viz.; (1) continuous submergence (5 ± 2 cm), (ii) continuous saturation (0—1 cm), (iii) continuous saturation+submergence at maximum tillering and flowering stages and (iv) alternate wetting and drying were assigned to main-plots and weed control treatments viz.; hand weeding twice at 20 and 40 days after transplanting, pre-emergence application of butachlor and thiobencarb liquid at the rate of 1.5 kg a. i./ha and thiobencarb butachlor and 2, 4—D (G) at the rate of 1.5 kg a. i. / ha, were kept in subplots. Weedy check was also included for comparison. The experiment was replicated thrice during both the years. The soil of experimental field was sandy loam in texture, with slightly alkaline reaction. The soil was low in available nitrogen and medium in phosphorus and potassinm. An uniform basal dose of 60 kg N, 60 kg P_2O_5 and 60 kg K_2O was applied at the time of puddling and remainder of 60 kg N was applied at maximnm tillering and flowering stages of crop growth. Rice variety IET 5725 was transplanted at row spacing 20 cm apart with plant to plant distance of 10 cm. Irrigation water was applied as per treatment. Under continuous submergence, 5 ± 2 cm standing water was maintained throughout crop growth by applying measured amount of water whenever needed. For maintaining continuous saturation crop was irrigated frequently to a depth of 1 cm. Under alternate wetting and drying condition crop was irrigated when small hair cracks appreaed in the field. The amount of irrigation water was measured with the help of a 7.62 cm

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parshall flume fitted in main irrigation channel. Herbicides were applied 4 days after transplanting. Granule herbicides applied by mixing with dry soil, while liquid formulation was applied with 'Maruti' foot sprayer. Granules were applied in 4 cm standing water. The liquid herbicide were applied after draining the field. Spraying of Dithane Z—78 and B. H. C. 5% dust was done to protect the crop from bacterial blight and rice gundhi bug, respectively.

Observations on weeds viz.; weed number, weeds dry matter accumulation and N. P. K. depletion by weeds were recorded at 30th, 60th and harvest stage of growth. Observations on crop plants viz.; plant height, dry matter accumulation, yield attributes, grain and straw yields and N. P. K. uptake were recorded wheat variety U. P. 262 was sown during rabi to study the residual effect of herbicide and observations were recorded on germinations count, weeds dry weight at harvest and grain yield of wheat. The salient features of the results thus obtained are summarised below :

Among different water management practices the continuous submergence was found most effective in minimising the number of weeds, weeds dry matter accumulation and N. P. K. depletion by weeds at all the stages during both the years. Continuous saturation and continuous saturation tsubmergence had similar effect on the growth of weeds. Both the treatments were significantly superior to alternate wetting and drying which recorded maximum value of weed number, dry weight of weed and N. P. K. depletion.

All the weed control treatments had significant effect on weeds growth over unweeded control which recorded maximum weed number, dry weight of weed and N. P. K. depletion of weeds. Treatment hand weeding (twice) was found most effective in minimising population of all type of weeds, weeds dry weight and N. P. K. depletion by weeds. Amongst herbicides, thiobencarb (L) followed by thiobencarb (G) were most effective in controlling weeds population and weed growth. These treatments were significantly superior to butachlor (L and G) and 2, 4—D (G) in minimising weed number, weeds, dry weight and N. P. K. depletion by weeds. The growth characters of rice viz.; plant height, tillers production, dry weight/hill, yield attributes, yield and N. P. K. uptake by crop were significantly higher under continuous submergence. Next to this, contnuous saturation + submergence was found most effective in respect of above characters and was at par with continuous saturation. Both the treatments were significantly superior to alternate wetting and drying condition which was found least effective and recorded poor growth, yield attributes, yield and nutrients uptake by crop.

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All the herbicides were found significantly superior over unweeded control in respect to growth, yield attributes, yield and N. P. K. uptake by crop. However, none of the herbicide could reach to the level of hand weeding which had significantly more growth, yield attribute, yield and nutrient uptake by crop. The herbicidal treatment thiobencarb (L) was found most effective and was at par with thiobencarb (G) and significantly superior to butachlor (L and G) and 2, 4—D (G). Among herbicides, 2, 4—D (G) recorded poor growth, yield attributes, yield and nutrient uptake by crop during both the years.

The effectivity of different weed control treatments varied with the variation in water management practices. In general, the granular formulation of herbicides was found most effective in minimising weed growth and increasing grain yield under continuous submergance. Whereas, the liquid formulation was found most effective in this respect in rest of water management practices irrespective of herbicides. Amongst herbicides, thiobencarb (G) was found most effective under continuous submergence in minimising crop-weed competition and producing maximum grain yield, while under rest of water management practices thiobencarb (L) was most effective herbicide in controlling weeds and enhancing crop yield. The performance of butachlor (L and G) was just after thiobencarb with different water management practices. Among herbicide, 2, 4—D (G) was found least effective as this treatment had more weed growth and low yield.

The irrigation use efficiency as expressed in terms of kg/ha mm of irrigation water applied was lowest under continuous submergence, while the maximum irrigation water use efficiency was noticed with alternate wetting and drying conditions during both the years.

The economics of each treatment was also calculated to draw the practical significance of the treatments.

Continuous submergence recorded maximum profit Rs. 2655.54 and Rs. 1984.50 during 1982 and 1983, respectively. Next to this treatment was continuous saturation which had net income Rs. 2565.74 and Rs. 1541.80 during 1982 and 1983, respectively. The minimum net return was recorded under alternate wetting and drying condition.

Use of herbicides had significant advantage over unweeded control as all the herbicidal treatments had more income than that of unweeded control. However, none of the herbicide could produce as much net return as hand weeding. Thiobencarb (L) followed by thiobencarb (G) recorded maximum income during both the years. The performance of butachlor (L and G) was just after thiobencarb. The lowest net income was obtained undr 2,

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4—D (G). The interaction effect between water management and weed control had significant effect on net income of the crop. The maximum return was recorded with hand weeding. Amongst herbicides, thiobencarb (G) gave maximum net return of Rs. 2869.20 and Rs. 2037.68 under continuous submergence during first and second year, respectively, while thiobencarb (L) was found most effective in rest of water management practices and gave maximum net return. The performance of all the herbicides under continuous saturation was just after continuous submergence. Herbicide butachlor (L and G) was found less profitable under continuous saturation + submergence as compared to rest of water management practices, while thiobencarb (L and G) and 2, 4—D (G) gave lowest net income under alternate wetting and drying condition. None of the herbicide showed any residual effect on succeeding wheat crop.

On the basis of the findings summarised in foregoing pages the following conclusions may be drawn.

1. Herbicide thiobencarb (L) followed by thiobencarb (G) were most effective in minimising crop weed competition and enhancing rice yield.
2. Thiobencarb (G) was found most effective under continuous submergence and gave maximum return, while under rest of water management treatments thiobencarb (L) recorded highest return among herbicides.
3. Continuous submergence (5±2 cm) was found to be most effective in reducing weed population, minimising nutrients losses and producing more grain yield followed by continuous saturation + submergence at maximum tillering and flowering stages.
4. The maximum irrigation water use efficiency was recorded under alternate wetting and drying and the minimum under continuous submergence.
5. None of the herbicides applied to rice crop had any adverse effect on succeeding wheat crop.

Recommendations :

On the basis of the conclusions drawn, the following recommendations can be made :

1. Granular formulation of thiobencarb or butachlor should be used under condition of continuous submergence.
2. Under continuous saturation or alternate wetting and drying conditions, the liquid form of thiobencrb or butachlor should be used for maximising rice production and net return.

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3. Under condition of adequate water availability continuous submergence (5±2 cm) throughout the entire period of rice growth should be maintained to harvest maximum grain yield and net return.
4. Under limited water availability, field should be maintained at continuous saturation so that the loss in yield and net return could be minimum.
5. Wheat crop can be safely grown as a rotational crop in *rabi* season after *kharif* rice where herbicides thiobencarb, butachlor and 2,4-D have been used.

STUDIES ON WEED CONTROL IN DRILLED UPLAND RICE IN RELATION TO NITROGEN APPLICATION

Vinod Kumar Srivastava Sup. *Dr. Mahatim Singh*

The present investigation entitled "Studies on weed control in drilled upland rice in relation to nitrogen application" was carried out at the Research Farm of the Department of Agronomy, Banaras Hindu University, Varanasi, during the *Kharif* seasons of 1979-80 and 1980-81 to study the relationship between applied fertilizer nitrogen and weed control measures in rice with an objective to explore the possibility of economising nitrogen fertilization without any yield reduction. Herbicides were compared with traditional hand weeding and unweeded control (weedy check). Wheat crop was succeeded on the same lay-out of experiment during the *Rabi* seasons of 1979-80 and 1980-81 to assess the residual effect of nitrogen levels and herbicides. The details of the experiments and results obtained are summarised hereunder.

Objectively the present experiment entails to study the efficiency of granular as well as liquid herbicides at varying levels of nitrogen for controlling the weeds in drilled paddy under dryland conditions. The experiment was laid out in a split plot design keeping the nitrogen levels in main plots and weed control treatments in sub-plots with three replications, Table 1. The study highlighted the possibility of economising the nitrogen dose without any reduction in grain yield, increasing the efficiency of nitrogen application by eliminating crop-weed competition with the use of chemical weed-killers.

The weed control efficiency was measured in terms of phytotoxic effects of various herbicides applied as pre-emergence, post-emergence, pre+

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post emergence as well as hand weeding treatment on weed population, dry matter accumulation and the amount of nitrogen depleted by weeds. Comparison of the effects of herbicides on crop characters related to number of tillers, number of leaves, dry matter production, uptake of nitrogen, grain yield and its components and protein content were studied in relation to manual weeding which provided a reliable measure of the selectivity as well as effectivity of herbicides.

The salient features of the research findings and broad conclusions derived from them are given below :

Herbicidal Effects

Weed Population :

Nitrogen incorporation brought out a marked variation on weed population in both the years of experimentation (Table 2 and 3). The weed population correspondingly increased with every increase in the rate of nitrogen in both the years being the maximum under highest rate of nitrogen (120 kg N/ha) and the lowest under control.

All the weed control treatments brought out significant reduction in weed population in both the years at all the stages of crop growth as compared to weedy check. Weed free plot remained completely devoid of dicot weeds with minimum number of monocots, during both the years. Treatments with pre and post emergence application of herbicides as in case of W_7, W_8, W_9 and W_{10} proved most effective in controlling weed population as compared to their individual application. The lowest weed population was recorded under the application of Butachlor+Propanil which proved superior to the rest of the combinations. Among the single application of herbicides the minimum weed population was observed under the post-emergence application of Propanil closely followed by Bentazon. Application of Bentazon and 2, 4-D were not much effective against the monocot weeds whereas the application of Butachlor was found least effective in controlling the dicot weed population.

Dry Matter Accumulation in Weeds

Dry matter production of weeds significantly increased with an increase in the level of nitrogen at all the stages of crop growth. An identical trend was observed in both the years. Significant reduction in dry matter accumulation in weeds under the weed control treatment was recorded over weedy check, however it was minimum under the hand weeding. Dry matter production suffered significantly under the combined application of Butachlor+Propanil and 2, 4-D+Propanil as compared to other herbicidal

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treatments. Among the single application of herbicides performance of Propanil was the best in reducing the dry matter content in weeds followed by Bentazon, Butachlor and 2, 4-D.

Depletion of Nitrogen by Weeds

Data on nitrogen depletion by weeds computed on the basis of dry matter content and percentage of nitrogen, Table 4.

Application of nitrogen appreciably increased the removal of nitrogen by weeds, the order of removal being $N_3 > N_2 > N_1 > N_0$. The pattern of nitrogen depletion by weeds was similar in both the years.

Nitrogen depletion by weeds showed marked variation due to weed control treatments in both the years at all the stages of crop growth. All the weed control treatments proved significantly superior to weedy check in this respect. Combined application of herbicides (pre + post) i. e. (W_7, W_8, W_9, W_{10}) established their profound effectivity in arresting the nitrogen depletion by weeds as compared to single application of herbicides (W_3, W_4, W_5, W_6). The maximum nitrogen depletion by weeds was recorded with 2,4-D application at each level of nitrogen dressing followed by the application of Butachlor. Propanil, however, proved the most effective in checking the nitrogen depletion closely followed by Bentazon.

Selective Effects

Dry Matter Accumulation by Rice Plants

Nitrogen fertilization enhanced the dry matter production in rice plants. Increasing levels of nitrogen application brought about significant increase in production of dry matter upto the second stage of the crop. Nitrogen application at the rate of 80 kg/ha proved superior to 120 kg N/ha at the concluding stage. These trends were found exactly the same in both the years, Table 5.

Dry matter production was significantly higher under all the herbicides application as well as in weed-free treatments as compared to weedy check, although weed free treatment showed maximum dry matter production, but remained statistically at par with all the combined application of herbicides during both the years at all the stages. All the combined applications of herbicides although remained at par among themselves but proved significantly superior over all the individual application of herbicides. Almost all the individual application of herbicides were statistically at par during both the years, however, the performance of Propanil was found the best in increasing dry matter production of rice crop closely followed by Bentazon, Butachlor and 2, 4-D.

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Number of Tillers and Leaves

The production of tillers as well as leaves were significantly increased by the nitrogen levels. Increasing rates of nitrogen proved instrumental in increasing the tillers as well as leaves upto the second stage of the crop. At the harvest stage 80 kg N/ha established its superiority over 120 kg N/ha in the production of tillers as well as leaves.

The number of tillers and leaves markedly increased under weed free and combined application of herbicides (W_7, W_8, W_9, W_{10}) over rest of the weed control treatments. Individually Propanil was the best treatment and produced higher tillers and leaves than Bentazon, Butachlor and 2, 4-D herbicides.

Nitrogen Uptake by Rice Crop

The uptake of nitrogen (kg N/ha) by rice crop was computed on the basis of percentage of nitrogen and dry matter produced, Table 6. Nitrogen incorporation brought about significant variation in nitrogen uptake at various crop growth stages. The maximum nitrogen uptake was recorded under 120 kg N/ha which was appreciably more than the other levels of nitrogen.

Weed control treatments produced significant improvement in nitrogen uptake as compared to weedy check in both the years. The combined applications of herbicides (W_7, W_8, W_9, W_{10}) and weed free treatment significantly enhanced the uptake of nitrogen over rest of the herbicidal treatments.

Yield Attributes

Yield attributes i. e., number of effective tillers, length of panicle, test weight of grains, number of filled grains significantly increased with increase in the rate of nitrogen application, Table 7. However, its expediency could be established only upto 80 kg, beyond which a slight decrease in these attributes was observed. Nitrogen at the rate of 120 and 80 kg although remained at par but proved markedly superior to 40 kg and the control.

Weed control treatments involving weed free condition as well as combined application of pre+post emergence herbicides, although proved equally effective in increasing the number of effective tillers, test weight, length of panicle, number of filled grains, however, registered their distinct superiority over the individual application of herbicides and weedy check in both the years. Among combination of herbicides, performance of Butachlor + Propanil was found the best, whereas among individual appli-

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cations response of Propanil was found the most effective closely followed by Bentazon, Butachlor and 2, 4-D.

Marked variation in the production of filled grains was recorded due to the interaction effect of nitrogen and weed control treatments during second year whereas it showed marked effect on the production of unfilled grains in both the years.

Grain Yield

In general, there was significant increase in grain yield in the second year as compared to the first year, Table 8. The marked variation in grain yield was observed due to year effect.

Nitrogen levels had significant influence on grain production. Remunerative response of nitrogen was observed only upto extend of 80 kg N/ha. Beyond this, additional nitrogen incorporation upto 120 kg N/ha could not prove advantageous and remained at par with 80 kg N/ha in increasing the grain yield.

Quadratic response function was worked out on the basis of pooled yield of two years and equation, $Y = a + bx + cx^2$ was fitted. Considering the output and input relationship the most profitable rate of nitrogen application was worked out to be 59.96 kg N/ha, although the maximum grain yield was obtained with 95.60 kg N/ha.

The grain yield was significantly more under all the herbicidal and weed free treatment as compared to weedy check. The maximum grain yield of 20.78 and 26.20 q/ha as recorded under weed free treatment in first and second year, respectively. Grain yield of rice was greatly enhanced under the influence of Butachlor + Propanil, 2, 4-D + Propanil, Butachlor + Bentazon and 2, 4-D + Bentazon as compared to the remaining treatments and were quite comparable to the weed free treatment. Next in order of superiority was Propanil, Bentazon, Butachlor. However, 2, 4-D proved to be the least effective.

Under respective levels of nitrogen all the combined application of herbicides significantly increased the grain yield over their individual applications.

Economics of Treatments

Application of Butachlor + Propanil and 2, 4-D + Propanil worked out to be the most profitable weed control treatments securing remunerative returns over weedy check as well as weed free treatments irrespective of nitrogen application during both the years whether it was dry or wet. Post-

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emergence application of herbicides i. e. Propanil and Bentazon were able to give an additional income over hand weeding only during 1980-81, whereas, pre-emergence application of herbicides i. e. Butachlor and 2, 4-D were not able to give any additional income during both the years.

Residual Effects of Herbicides

None of the herbicides applied in rice for controlling the weeds left any residues to affect the germination and grain yield of wheat grown immediately after the rice harvest.

Conclusions

On the basis of the present investigation results summarized in the foregoing pages, the following broad conclusions may be drawn :

(1) For efficient utilization of applied nitrogen the weeds should be kept under check either by combined application of herbicides Butachlor/ 2, 4-D/Propanil/Bentazon or weed free treatment (hand weeding).

(2) The removal of nitrogen through weeds was considerably arrested by weed control treatments. At the harvest stage it was 35.0 kg/ha during 1979 and 19.31 during 1980 under unchecked weed growth as compared to 1.16, 4.03, 4.47, 4.84, 5.55 kg/ha during 1979 and 0.59, 1.11, 2.08, 2.14, 2.93 kg/ha during 1980 under weed free, Butachlor + Propanil, 2, 4-D + Propanil, Butachlor + Bentazon and 2, 4-D + Bentazon, respectively.

(3) The most profitable rate of nitrogen application was worked out to be 59.96 kg/ha for rice (Var. Cauvery), although the maximum grain yield was obtained with the application of 95.60 kg N/ha.

(4) Pre-emergence application of Butachlor + Post-emergence application of Propanil proved to be the most effective for controlling monocot. as well as dicot. weeds in rice field.

(5) Incorporation of nitrogen played profound influence on the effectivity of herbicidal application. By and large, combined application of Butachlor + Propanil not only proved most effective in controlling weeds but showed marked increase in its effectivity with every increase in rate of nitrogen. This was found true with other herbicides as well. At lower rates of nitrogen application, it is recommended to apply 2, 4-D + Propanil, Butachlor + Bentazon and 2, 4-D + Bentazon for effective control of weeds, whereas with higher nitrogen dressing herbicide like Propanil, may also be used.

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(6) Application of Butachlor + Propanil and 2, 4-D + Propanil were found economical over hand weeding during both the years whether it was dry year or wet year.

(7) None of the herbicides applied either pre or post emergence in rice crop left any residues in the soil to affect adversely the succeeding crop of wheat.

UTILIZATION OF BUTTERMILK FOR THE MANUFACTURE OF CHHANA-BASED SWEETS

Vijay Shanker Pandey Sup. *Dr. V. N. Bhargava*

Buttermilk constitutes an important milk by-product in the country. A large part of its huge quantity available at present is not put to profitable use and is wasted at present. As such the present study entitled "Utilization of buttermilk for the manufacture of chhana-based sweets" was undertaken which comprised four phases :

Phase I was devoted to study the effect of varying the calcium content of buttermilk on the production of chhana and whey. The effect on chhana judged in terms of :

(i) Yield,
(ii) Chemical composition,
(iii) Sensory characteristics, and
(iv) Rheological properties.

For whey only the first two variables were taken into account. This phase included five replications each involving four levels (700-800, 900-1000, 1100-1200 and 1500-1600 ppm) of calcium in buttermilk used for making chhana.

Phase II entailed five replications. Each was carried out to know the effect of admixing 0, 10, 20, and 40 per cent of standardized cow milk (3.5% fat) with 100, 90, 80 and 60 per cent of cows' sweet-cream buttermilk, respectively, on the yield and qualities of chhana, rasogolla, sandesh and chhana-whey in comparison to those obtained from fresh cow milk.

Phase III consisted of four replications. Each was devoted to study the effect of mixing 0, 20 and 40 per cent of standardized cow milk with 100, 80 and 60 per cent of buffaloes' sweet-cream buttermilk, respectively, on the yields and qualities of the aforesaid four products in comparison to those obtained from fresh cow-milk.

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Phase IV was a duplicate of the III phase except that in this phase, desi buttermilk (prepared from cow-dahi) was used in place of buffaloes' sweet-cream buttermilk.

The qualities of chhana, resogolla and sandesh were evaluated in terms of :

(a) Chemical composition,

(b) Sensory characteristics,

(c) Rheological measurements in respect of springiness and penetration value, and

(d) Consumer acceptability (excluding chhana).

In case of whey only the chemical composition was taken into consideration.

Methods and Materials

In the I and II phases, buttermilk prepared from cows' sweet-cream (40% fat) without addition of breakwater was used for experimentation. In the III phase, buffalo buttermilk obtained from sweet-cream (40% fat) was used. For the IV phase, desi buttermilk was used. For preparing this, 2 parts of dahi (2-2.5% acidity) were mixed with 1 part of water and churned. Cow milk with 4.5 per cent fat was used for making dahi.

The calcium concentration in buttermilk was varied by adding 5% solution of calcium chloride at the rate of 0, 10, 20 and 40 ml per kilogram of buttermilk in the four groups of the first phase. Fresh cow milk standardized to 3.5 per cent fat was used for admixing with different types of buttermilk. Chhana was prepared by using 0.8 per cent citric acid solution for coagulation at pH 5.4 and the procedure given by De and Ray (1954) was followed. Desi buttermilk was neutralized to pH 5.4 by adding 30% solution of sodium hydroxide before adding milk and before coagulating.

For making rasogolla procedure recommended by Bhattacharya and Desraj (1980a) was followed, and sandesh was prepared as per method stated by De (1976).

Chemical analysis of buttermilk, chhana, rasogolla and sandesh were done according to method laid down in IS : 1479 (Part II, 1961); IS : 5162 (1969); IS : 4079 (1967); and IS : 5550 (1970) respectively. Springiness of products was determined by method given by Gera and Rajorhia (1979) and hardness of milk products was measured using penetrometer as per procedure given in A. O. A. C. (1964). Consumers reactions towards these sweets were determined on hedonic scale (Nelson and Trout, 1964. p. 453) by assigning numerical scores varying from 10 (like extremely to 2 (dislike extremely).

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Results

Part I : *Yield and Quality of Chhana Obtained From Buttermilk*

Fresh as well as dry yields of chhana increased significantly when the level of calcium in buttermilk was raised from 750 to 950 ppm. Further addition of calcium did not have a favourable effect. Increased recovery of total solids in chhana at 950 ppm calcium in buttermilk was responsible for increased yield of chhana.

Increasing the mean level of calcium in buttermilk to 950 ppm did not deteriorate the physical quality of chhana substantially. Higher level of calcium (1140 and 1550 ppm) on buttermilk imparted a chalky taste in chhana and made its body hard.

These results suggested that for optimum quality and yield of chhana, the calcium concentration in cow-buttermilk should be between 900 and 1000 ppm.

Effect of addition of cow milk in buttermilk on production of chhana

The mean percentage of total solids in the II phase in cow milk, cow-cream buttermilk, and cow-cream buttermilk containing 10, 20 and 40 per cent of standardized milk were estimated as 12.11, 7.90, 8.19, 8.70 and 9.82, respectively, and the corresponding mean values for fat content were 3.50, 1.12, 1.50, 1.80 and 2.50 per cent. Similarly in the III phase the concentrations of total solids in cow milk, buffalo-cream buttermilk, and in buffalo buttermilk containing 20 and 40 per cent of standardized milk were 12.21, 9.06, 9.80 and 10.11 per cent, respectively, and the corresponding mean percentages of fat were 3.50, 1.15, 1.70 and 2.03. In the IV phase mean percentages of total solids in cow milk, desi buttermilk, and desi buttermilk containing 20 and 40 per cent of milk were 12.14, 6.60, 7.46 and 8.56 respectively and the corresponding mean percentages of fat were 3.50, 0.53, 0.95 and 1.58. The concentrations of total solids and fat in all the three types of buttermilk were significantly less than those in the cow milk. Addition of milk in different buttermilks raised the contents of fat and total solids significantly.

However, despite 40 per cent addition of milk in butter-milk, the concentration of total solids and fat remained significantly lesser than their counterpart in standardized cow milk.

The mean yield of fresh chhana from cow-cream buttermilk was 12.57 per cent in comparison to 16.22 per cent from standardized cow milk, and when expressed on moisture-free basis the corresponding yields worked out to 3.11 and 6.35 per cent. Similarly the dry yields of chhana from buffalo-cream buttermilk and desi buttermilk were found significantly less than

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that from standardized cow milk. Admixture of cow milk with all the three buttermilks has been found to increase the yield of chhana. Besides, the yield of chhana from cows' desi-buttermilk was found invariably lower than that obtained from cows' sweet-cream buttermilk which might be due previous curdling of milk. The yield of chhana has been found to be a function of concentration of total-solids in the raw material. Similarly a close association between fat level in the raw material and the yield of chhana has been established. Within the range of percentages of total solids or fat in fluid studied, positive linear relationships between the yield of dry chhana and the percentage of total solids in the fluids used, and between the yield of dry chhana and the percentage of fat in fluid, have been found. Using these relationships, separate regression equations have been developed to predict yield of chhana from concentration of fat or total solids in the raw material.

Chhana samples prepared from cow-cream buttermilk, buffalo-cream buttermilk and *desi* buttermilk on average had 7.51, 6.12 and 4.75 per cent fat, respectively which were significantly lesser than that in cow-milk chhana. Fat content in chhana showed an upward deviation with progressive addition of milk in buttermilk. Average protein content was however, higher in all buttermilk chhana than cow-milk chhana.

The percentages of total solids in chhana prepared from cow-cream buttermilk, buffalo-cream buttermilk and cows' *desi* buttermilk averaged 24.71, 24.50 and 25.89 respectively and these were found to be significantly less than that of cow-milk chhana. Total solids in chhana increased significantly with incorporation of standardized milk in buttermilk, and the moisture content of chhana demonstrated, a reverse trend. Moisture content in chhana has been found to have an inverse relationship with the concentration of fat in chhana. Based on this relationship a simple linear regression equation has been derived which can be used to predict the percentage of moisture in chhana from the fat content of the milk or buttermilk satisfactorily at least within the limits of fat percentages included in this study.

The averages for the recovery of fat in chhana were 84.16 per cent from cow-cream buttermilk, 85.43 per cent from buffalo-cream buttermilk and 62.38 per cent from cows' desi-buttermilk, and these were significantly less than that obtained form the cow milk. Fortification of buttermilk with milk tended to push up the recovery of fat from the two sweet-cream buttermilk but not from desi buttermilk. This may be ascribed to poor coagulation of proteins in the form of flakes in case of *desi*-buttermilk. The recoveries of protein and total solids in chhana also indicated similar trends.

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Sensory scores of buttermilk chhana, especially that of *desi*-buttermilk chhana, were low in comparison to that of cow-milk chhana. Fortification of creamery buttermilk with milk considerab'y improved the organoleptic qualities of chhana. However, it was not so in case of *desi*-buttermilk chhana in which the gluey flavour and gummy texture though decreased but persisted even after 20 per cent enrichment with milk.

Chhana samples prepared from buttermilk were less spongy than cow-milk chhana. Addition of milk in sweet-cream buttermilk improved the springiness of chhana considerably. The chhana samples made from sweet-cream buttermilk were not much different in hardnees as compared to cow-milk chhana. Howewer *desi*-buttermilk chhana was significantly harder than cow-milk chhana. Despite low fat content, the chhana samples obtained from the sweet-cream buttermilk especially those obtained after 20 per cent or more addition of milk, had soft and spongy body.

Part II : *Production of Chhana-whey from buttermilk*

Increasing the mean concentration of calcium in buttermilk from 750 to 950 ppm or more increased the yield of chhana whey significantly which was attributed to better aggregation of casein molecules and formation of firmer curd leading to greater exudation of whey. The percentages of total solids and protein in whey were minimum when the cow-cream buttermilk contained 900-1000 ppm of calcium.

The outputs of whey from creamery buttermilk and from cow-milk exhibited no significant difference. However, whey yield was comparatively less from desi buttermilk mostly as a result of lesser amount of coagulant used. Chhana-whey obtained from all the three types of buttermilk had lower percentages of total solids, fat and lactose than in that prepared from cow milk.

Protein content was, however, higher in whey obtained from buttermilk than in the whey produced from cow milk. Ash content of buttermilk wheys was not significantly different from that of cow-milk whey. Addition of milk in buttermilk tended to increase the fat content in whey. The protein content in whey obtained from sweet-cream buttermilk did not increase with addition of milk in buttermilk, but it showed marked elevation with 40 per cent addition of milk in *desi* buttermilk.

Part III : *Production of Rasogolla from buttermilk*

The mean yields of fresh rasogolla per 100 gram of cow-cream buttermilk, buffalo-cream buttermilk and *desi* buttermilk were estimated to be 30.04, 43.57 and 19.72 gram, respectively. The percentage yields of raso-

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golla from cow-cream buttermilk and cows' *desi*-buttermilk were significantly less than the yield obtained from cow milk (3.5% fat). Yield of rasogolla showed a marked increase with 40 per cent addition of milk in cow-cream buttermilk. In case of *desi* buttermilk the rasogolla disintegrated during boiling with 40 per cent fortification of buttermilk with milk. Incorporation of milk in buffalo-cream buttermilk did not influence the yield of rasogolla significantly. The results indicated that the yield of rasogolla was markedly associated with the percentages of fat and total solids in the fluids used, and could be predicted satisfactorily using the regression of rasogolla-yield on the percentage of fat in fluid or on the percentage of total solid in the fluid.

Moisture content in rasogolla obtained from the three buttermilk did not show any significant fluctuation with the addition of milk. However, fat content was lower in buttermilk rasogollas than in the cow-milk rasogolla, and increasing addition of milk in buttermilk progressively increased the richness of rasogolla in respect of fat. Mean concentrations of protein, carbohydrates and ash in rasogollas prepared from the three buttermilk did not differ significantly from those of cow-milk rasogolla, and addition of milk in any of these buttermilk did not significantly alter these.

Addition of milk in all the buttermilk resulted in slightly lesser retention of fat in rasogolla. The loss of fat during rasogolla making was greater when *desi*-buttermilk was used.

Organoleptically the buttermilk rasogollas were slightly inferior to cow-milk rasogolla. Increase in proportion of milk in sweet-cream buttermilk made a linear improvement in the sensory score of rasogolla and with 40 per cent inclusion of milk in these two buttermilk the sensory quality was found somewhat superior even to that of cow-milk rasogolla. In case of desi buttermilk even after 20 per cent incorporation of milk, the rasogolla had inferior quality.

Whereas, rasogolla obtained from cow-cream buttermilk and *desi* buttermilk had lower springiness than cow-milk rasogolla, the springiness of buffalo-buttermilk rasogolla was not significantly different from that of cow-milk rasogolla.

Penetration values of rasogolla, made from the three types of buttermilk were lesser than that of cow milk rasogolla.

Rasogollas made from cow-cream buttermilk were slightly liked by the consumers, those obtained after 10 per cent inclusion of milk in cow-cream buttermilk were moderately liked, and those prepared after 20 and 40 per cent enrichment of buttermilk (cow-cream) were liked very much quite

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equal to the cow-milk rasogolla. Similarly, the buffalo buttermilk after 20 per cent enrichment with milk gave rasogollas of high acceptability, and with 40 per cent incorporation of milk the acceptability was even higher than that of cow milk rasogolla. The rasogolla prepared from *desi* buttermilk enriched with 20 per cent of milk had low acceptability. It is, therefore, likely that certain beneficial alterations in salt balance and protein behaviour might have taken place during rasogolla making from sweet-cream buttermilk, which had overshadowed the compositional limitations, of these raw materials.

Part IV : *Production of Sandesh from buttermilk*

The mean yields of *sandesh* from all the three buttermilks were found significantly less than that obtained from cow milk. Yield of *sandesh* from buttermilk increased with the increase in concentrations of total solids and fat in the raw material. Yield of *sandesh* has been found to be a function of percentage of total solids and fat content of the fluid (buttermilk and/or milk).

Mean moisture of cow-milk sandesh was found significantly less than those of sandesh prepared from the three buttermilk. Addition of milk in buttermilks decreased the moisture content in sandesh. Fat content of sandesh exhibited a reverse trend.

Recoveries of fat in sandesh from the two cow buttermilk were less than that from the cow milk.

Organoleptically, *sandesh* prepared from the three buttermilk were slightly inferior to cow-milk *sandesh*. However, minimum inclusion of 20 per cent of milk in any of these buttermilk was found to yield *sandesh* having moderate acceptability.

Thus, it will be appropriate to conclude that both cows' sweet-cream buttermilk and buffaloes' sweet-cream buttermilk with 20 per cent incorporation of milk in each, were found suitable for preparing rasogolla and *sandesh* of acceptable quality. *Desi* buttermilk under the conditions of these experiments could not yield rasogolla of good quality, however, it was found suitable for preparing *sandesh* after 20 per cent fortification with milk. It needs no emphasis that utilization of buttermilk in this way, if translated into practice will certainly spare a large quantity of fluid milk for direct consumption, which is presently utilized for production of sweets.

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POPULATION DISTRIBUTION OF SOME IMPORTANT ANTHROPOD PESTS OF APPLE AND THEIR MANAGEMENT BY CHEMICALS IN KASHMIR VALLEY

Gulam Ahmed Dar Sup. *Dr. H.N. Singh*

Apple is one of the most important commercial crop all along the foot-hills of Himalaya. It is subject to attack, in field, by a number of arthropods including San Jose scale, aphids, beetles, mites, leaf feeders and stem borers. The pest complex varies, both in composition and economic status, with the agro-climate from place to place within this country. The prevalent control practices are restricted to application of dormant sprays with diesel oil against San Jose scale which is the most serious pest in the Northern India. Little is known on the field efficacy of the common synthetic insecticide against the pest complex and no information exists on the background knowledge of various pests necessary to evolve a common and effective chemical control schedule in Kashmir valley.

Accordingly, the pest fauna, their seasonal activity, population distribution and the time of prevalence of insecticide sensitive stages were determined and also, the field efficacy of a number of chemical spray schedules against the pest complex was compared in present study at Fruit Research Station, Shalimar, during the years 1981 and 1982 on ten year-old bearing apple trees of Red Delicious variety with semivigorous root stock having moderate San Jose scale infestation.

The experiment was laid out in randomised Block Design in three replications with single tree as a plot. Each of the six insecticides, namely monocrotophos, quinalphos, carbaryl, methyl demeton, endosulfan and diesel oil, were applied thrice separately at first male emergence (Schedule A), first generation crawler emergence (Schedule B) and second generation crawler emergence (Schedule C). These along with their combinations (Schedules AB, AC, BC, ABC), formed, in total, 42 treatments plus an untreated control to occupy 129 trees in a homogeneous apple orchard. Parameters for recording monthly pest population were number of live San Jose scales per 5 cm twig or per leaf, aphids and mites per leaf and per cent mined leaves. Calculation of degree-days were based on the temperature and scale development relationship studies of Rice *et al.* (1982 a). The salient observations are summarised below :

(1) The insect and mite complex on apple comprised of San Jose scale (*Quadraspidiotus perniciosus* Comst.), spirea aphid (*Aphis spiraecola* Patch.), woolly apple aphid (*Eriosoma lanigerum* Hausm.), apple leaf miner

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(*Lyonetia clerkella* L.), European red mite (*Panonychus ulmi* Koch.) and false spider mite (*Cenopalpus pulcher* C & F). Presence of spirea aphid and European red mite signifies their first record from Kashmir valley.

(2) These pest species were active throughout the apple season from March-April to October-November except for *L. clerkella* which was active from middle of April to first week of June.

(3) Peak population of scale on untreated twigs during 1981 was 81 scales/5 cm twig in October that rose during 1982 to 231 scales/5 cm twig in September. Scales, on leaves, reached to maximum in October being 16 and 52 per leaf during the two years, respectively. The unsprayed trees had 95 and 93.3 per cent fruits infested with scale in September of both the years, respectively.

(4) Damage of apple leaf miner reached its peak by first week of June during both the years. Majority of leaves (66.1% during 1981 and 70.8% during 1982) showed 2 to 4 mines per leaf. The highest number of mines per leaf was recorded to be 17. Peak population of *P. ulmi* during both the years was recorded during September being 3.00 and 4.50 mites/leaf, respectively. Spirea aphid population during 1981 was highest in June (34.7/leaf) and during 1982, in May (22.3/leaf). The woolly aphid met highest number of colonies per tree during September in both the years being 6 and 13.3 for the respective years.

(5) Life stage studies on scale recorded male emergence, from overwintered population, to start on 17th April during 1981 and 25th April during 1982. The first generation crawlers, from gravid females put under examination, started emerging on 16th May, 1981 and 25th May, 1982. The interval between the start of male emergence and that of crawler from overwintered scales was 30 and 31 days during the two years, respectively This interval reconciled well with the accumulated days between the male and crawler emergence.

(6) San Jose scale at Shalimar had two complete and a third overwintering generation in a year. Highest number of crawlers was laid by first summer generation females showing an average of 178 nymphs/female, and the least number was met with the second summer generation females with an average of 62.4 nymphs/female. Parturition period varied from 31 days in case of overwintered females, to 62 days in case of second generation, females.

(7) Toxicity of insecticides against San Jose scale did not vary significantly among different months of treatment. Scale mortality recorded after a month of spraying reached upto 100 per cent in case of quinalphos

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which proved to be the most effective insecticide. Diesel oil with 42.5 per cent mortality proved to be the least toxic. Similar toxicity trends were observed even at harvest. Effect of spray schedules against scale, at harvest, was nonsignificant during 1981. But during 1982 schedule AB, involving spray against male emergence and first crawler emergence, gave overall better performance as compared to other six schedules.

(8) All the spray schedules which incorporated spray treatment coinciding San Jose scale male emergence in April, gave effective control of the leaf miner during both the years. Among the insecticides, during 1982, the diesel oil emulsion, with 27.67 per cent leaf damage, proved to be less effective than endosulfan showing 13.48 per cent leaf damage. The latter was at par with monocrotophos (15.26%), methyl demeton (18.14%) and quinalphos (19.75%). The insecticides were similar in response during 1981.

(9) European red mite population during 1981 was lower on plants treated with monocrotophos as compared to methyl demeton and quinalphos. Rest of the treatments were at par with monocrotophos. The efficacy order during 1982 was: monocrotophos = methyl demeton > quinalphos > carbaryl > diesel oil emulsion > endosulfan recording 0.932, 0.975, 1.346, 1.508, 1.666 and 1.877 mites per leaf, respectively. Among the schedules, AC gave better results. Insecticidal as well as schedule effects were non-significant in case of false spider mite during both the years.

(10) All the insecticides afforded better control of spirea aphid and woolly aphid as compared to untreated control. The insecticide and schedule effects proved to be nonsignificant during both the years in case of spirea aphid and during 1981 in case of woolly aphid. During 1982 carbaryl was found to be the least effective in reducing woolly aphid population and schedule AC, being at par with schedule B, proved to be the least effective against this aphid.

(11) A simple technique was evolved to detect male and crawler emergence in San Jose scale under field conditions. A new approach for forecasting the dates of male and crowler emergence from overwintered scale population was described based on degree-day accumulation,

(12) The experimental findings have been compared with the available literature. It has been concluded that application of 0.05 per cent quinalphos twice, coinciding with scale male emergence in April and crawler emergence in May would effectively control the various arthropod pests of apple in general in Kashmir valley. The occurrence of these two sensitive stages could be precisely forecasted, well in advance, by the help of a degree-day chart.

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ENTOMOLOGY & AGRICULTURAL ZOOLOGY

RICE LEAP AND PLANT HOPPERS IN RELATION TO PADDY VARIETIES AND ABIOTIC FACTORS

Keshav Reddy Dharma Reddy Sup : *Dr. D. S. Mishra*

The investigations on 'Rice Leaf and Plant Hoppers in Relation to to Paddy Varieties and Abiotic Factors' were carried out during 1981 and 1982 at Agricultural Research Farm, Banaras Hindu University, Varanasi, with the following objectives :

1. To study the response of various rice varieties to rice leaf and plant hoppers under field and cage house conditions.
2. To measure the honey dew excretion by major rice leaf and plant hoppers in order to assess the resistance of rice varieties.
3. To assess the role of bio-chemical components of rice plant in affecting rice leaf and plant hopper population.
4. To know the spatial distribution pattern of some important rice leaf and plant hoppers.
5. To record the relationship between the population densities of commonly occurring leaf and plant hoppers and abiotic factors.
6. To find out the correlation, if any, between the population of rice leaf and plant hoppers recorded with the help of light trap and from the field.

The cage house experiments were conducted at C.R.R.I., Cuttack. The results of these studies are summarised below :

(1) The experiment on performance of various rice varieties against *Nephotettix* spp., *Nilaparvata lugens* and *Sogatella furcifera* was made both under field and cage house conditions. The experiments conducted under cage house conditions were preference, screening, nymphal survival and honey dew excretion. Biochemical components such as soluble carbohydrates, phenols and amino acids of various varieties were also analysed in reference to these hoppers. However, the response of *Recilia dorsalis*, *Tettigella spectra* and *Nisia atrovenosa* was studied only under field conditions.

The resistant check Ptb 33 and the susceptible check TN 1 performed as expected, in the present study, i. e., the former recorded the least population, produced less honey dew area and showed low damage rating, pre-

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ference and nymphal survival, while the latter recorded high levels of all these parameters. Among the test varieties the ones that showed promise were : IR 8, Jaya and OR 34-16 for *Nephotettix* spp., Culture 1, IR 28 and IR 8 for *N. lugens*; Culture 1, *Jelhore* and IR 28 for *S. furcifera* and IR 8 and IR 28 for *R. dorsalis*, *T. spectra* and *N. atrovenosa.* However, the performance of even these varieties was significantly less than that of resistant check (Ptb 33). The remaining varieties did not give any conclusive inference. The total soluble sugar percentage appears to be low in resistant varieties and high in susceptible varieties, whereas, percentage of total phenols and amino acids gave no conclusion.

The period for peak population of all these hoppers differed from species to species but, in general, occurred between 37 DAT and 72 DAT (Days after transplanting) during both the years.

The total leaf and plant hopper population and the resulting yield loss varied in different varieties, but were more pronounced in the year 1982 than in 1981. However, the yield loss in Ptb 33, IR 28, IR 8, Culture 1, OR 34-16 and *Jelhore* was less in comparison to the remaining varieties during both the years.

(2) Spatial distribution pattern of *Nephotettix* spp., *S. furcifera* and *N. lugens* was recorded from 180, 160 and 150 sample at 51, 52 and 53 DAT, respectively, in the field of variety IET 5725. The data were computed for their spatial distribution following the methods of detection of dispersion by using frequency distribution, statistic U and statistic T tests for agreement with a negative binomial distribution. indices of dispersion and the variance-mean relationship. The details of these methods are described in Chapter 3.

Studies on the micro-distribution of leaf and plant hoppers in rice field exhibited negative binomial pattern, showing clumped or aggregated nature of infestation.

(3) The population fluctuation of rice leaf hoppers and plant hoppers recorded with the help of light trap revealed that *N. virescens* was numerically the most abundant species that constituted 82.17 per cent of the total leaf and plant hoppers population under light trap during both the years. The dominance of remaining species was in the order of *N. nigropictus* (9.69%), *S. furcifera* (4.03 %), *N. lugens* (3.10%), *R. dorsalis* (0.66% *T. spectra* (0.17%) and *N. atrovenosa* (0.14%). The first occurrence of *N. lugens* and *T. spectra* in the first fortnight of June; *N. nigropictus*, *N. atrovenosa* and *N. virescens*, *R. dorsalis* either in the first or in second fortnight of July were recorded during both the years. Further, all these

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hoppers disappeared either in the month of November or December each year.

In general, *N. lugens* has occurred for maximum period, i. e., 27 & 29 weeks in light trap and was followed by *S. furcifera, T. spectra, N virescens N. atrovenosa, N. nigropictus* and *R. dorsalis* for 25 & 27, 25 & 26, 24 & 25, 23 & 24, 21 & 23 and 18 & 19 weeks, during both the years, respectively. The frequency of emergence of these hoppers on light trap were in the descending order of *N. virescens, S. furcifera, N. lugens, N. nitropictus, T. spectra, N. atrovenosa* and *R. dorsalis.* However, the relative frequency of these hoppers was high during 41st and 44th standard week during both the years.

The maximum mean population of leaf hoppers was observed in the last fortnight of October during both the years, whereas, maximum plant hoppers were recorded in the last fortnight of October and first fornight of November during 1981 and 1982, respectively.

Different statistical methods were also applied to detect the pattern of emergence in light trap that exhibited irregular pattern. The fiducial intervals at 95 per cent probability level confirmed the pronounced variation in daily trap catches.

The multiple correlation coefficient (R) between the individual hopper population and abiotic factors exhibited highly significant positive influence at 1 per cent level of probability, except *N. lugens* which was significant only at 5 per cent probability level. The value of coefficient of determination (R^2) highlights the joint contribution of abiotic factors on the light trap catches of each of rice leaf and plant hoppers which was less than 50 per cent. Further, regression coefficient (bi's) analysis with *N. virescens, N. nigropictus, R. dorsalis, T. spectra, N. lugens, S. furcifera* and *N. atrovenosa* exhibited significant positive correlation with mean temperature and significant negative correlation with average relative humidity and evaporation.

Correlation (r) between the field population and rainfall exhibited significant negative correlation at 5 per cent probability level with *Nephotettix* spp. and *N. atrovenosa*, whereas, *N. lugens* with temperature and *N. atrovenosa* with sunshine hours recorded highly significant positive correlation at 1 per cent probability level. The remaining species of rice leaf and plant hoppers failed to establish any relationship.

Correlation (r) between light trap cttches and the population from varietal field, Pusa 33 and Jaya revealed that only *Nephotettix* spp., recorded from Jaya field, exhibited significant positive correlation with the population of light trap, whereas, rest of the species did not show any significant correlation.

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STUDIES ON IMPORTANT INSECT PESTS IN CERTAIN CULTIVARS OF *CAJANUS CAJAN* (L.) MILLS AND THEIR CONTROL

Anumula Ranga Reddy Sup : *Dr. H. N. Singh*

Pigeonpea is an important pulse crop grown in India for its multiple uses as a source of food, feed, fuel and fertilizer. One of the important factors of low production in this crop is the loss caused by insect pests to this crop amounting some times to more than 40 per cent. Pigeonpea in the field is attacked by more than 120 insect species including some serious pests like the hemipteran pod bug (*Clavigralla gibbosa)*, lepidopteran pod borers like legume pod borer (*Maruca testulalis*), plume moth (*Exelastis atomosa*), blue butterfly (*Euchrysops cnejus*), leaf webber (*Cydia critica*), gram pod borer (*Heliothis armigera*), dipteran podfly (*Melanagromyza obtusa*) and coleopteran pulse beetle (*Callosobruchus chinensis*). The pest problem varies among different agroclimatic regions within the country. The pest severity is also affected by the cultivars maturity duration, growth habit and genetic susceptibility to individual pests.

Application of insecticides is the only solution at hand to save the crop from being damaged. There is a need for evolving a suitable insecticide which is ecologically sound, economically feasible and socially acceptable. The long term pest management practices envisage studying hitherto unexplored population distribution, conditions favouring pest abundance, plant character affecting pest incidence and screening germplasms less susceptible to at least the serious pests of the region.

Studies on population distribution of important insect pests, their resistance among promising cultivars and the effect of certain insecticidal treatment schedules on pigeonpea were carried out in separate lay outs at the Agriculture Farm of Banaras Hindu University, Varanasi during the years 1981-82 and 1982-83 under Randomized Block Design and Factorial R.B.D. with 3 replications. The salient findings are summarised below :

1. Seasonal population studies indicated the economically important pests to be the podfly, pod bug, plume moth and blue butterfly. The pod bug was most serious in early cultivars whereas the maximum damage in late cultivars was caused by the podfly. The medium maturity cultivars were affected both by pod bug as well as podfly. The two borer species proved to cause significant damage with respect to pod infestation, seed injury and grain weight loss. The number of flushes in six cultivars representing early, medium and late cultivars and determinate and indeterminate growth habits varied from 2 to 4 flushes. All the maturity groups

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of determinate growth habits showed from flushes whereas those of indeterminate habit underwent two flushes. Duration of flush in each cultivar was influenced by prevailing temperature. The total yield of all the flushes was higher in determinate types compared to the other group. Opposite was true when the yield measurements were restricted to the first flush only.

2. Population of each of the pest studied followed two peaks during the crop season. The first in case of podfly occurred between 46th to 6th standard week and the second two weeks later. Larval population of podfly varied from 0 to 120 during first year and 6 to 207 during second year on various cultivars. The bug population became insignificant during extreme winter between 50th to 8th week thus giving rise the two peaks having population ranging from 0.00 to 319.00 and 0.00 to 240.00 in the first and second years respectively. The population of plume moth and blue butterfly formed first peak rise from 46th to 52nd and the second after 8th week, the first being the major than the later. The population of plume moth ranged from 0.00 to 66.33 in first year and 0.00 to 56.67 in second year. The larval population of blue butterfly varied from 0.00 to 131.33 and 0.00 to 175.33 in the first and second years respectively.

3. The initial flush of early cultivars harboured lowest podfly population which reached to maximum in late cultivars, there being no difference in podfly population in latter flushes, Higher bug population was recorded on early cultivars compared to medium and late ones during the first flush. The opposite was true during the last flush. Highest population of plume moth larvae was met with the early cultivars whereas the blue butterfly was maximum in late cultivars. All determinate cultivars irrespective of maturity group harboured higher borer population compared to indeterminate except C-11. Podfly as well as the pod bug showed no distinction in population between two growth habits.

4. Screening of 11 early, 16 medium and 16 late maturity cultivars against the pest incidence indicated variation in relative susceptibility in respect to pod infestation and damage and grain weight loss. The susceptibility varied with the pest species. The cultivars shown lowest pod and seed damage and least weight loss against podfly consistently during both the years were ICPL-1 followed by ICPL-81 in early, GS-2 followed by BDN-1, BDN-2 from medium, MA-2 followed by JA-17 from late maturity groups. The less susceptible cultivars against pod bug were T-21 and ICPL-189 from early ICPH-2, GS-2 from medium and MA-95 followed by ICPL-310 from the late maturity group. Response among cultivars to borers was significant only in the years witnessing higher population in

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general ICPL-81 and T-21 among the early, AS-71-37, MA-39-2, ICPL-42 from medium and PDA-7 and G-2 from late maturity group were the least preferred cultivars against the borer complex. Lowest field infestation of pulse beetle was recorded in ICPL-6 followed by T-21 among early ICPH-5, GS-2 and ICPL-42 among medium and MA-95 and T-7 among the late maturing cultivars.

5. The cultivars which showed least total damage by all the pest complex in common during both the years consistently and promised respectful yield were identified to be T-21 and ICPL-189 from early ICPH-2 from medium and MA-2 from late maturity group. Yield parameters being inherent, their varietal character showed no relation with the damage parameters.

6. Relative efficacy of monocrotophos, dimethoate, quinalphos, endosulfan, cypermethrin and decamethrin each applied at two doses, one normally recommended and the other 1.5 times higher than that was tested under two spray schedule, the first comprising of single treatment and the other with two treatments at 15 days interval. The results indicated insecticidal specificity among the insect species. In general organophosphorus insecticides like monocrotophos and dimethoate proved more efficaceous against podfly. Endosulfan followed by both the synthetic pyrethroids were selectively more effective against pod bug and lepidopteran borer complex compared to organophosphorus insecticides.

7. Lower pod infestation, seed damage and grain weight loss were observed at higher dose compared to lower dose irrespective of insecticides. Two spray schedule was proved more effective to reduce various damage parameters compared to one spray schedule. Monocrotophos applied twice @ 0.600 kg a.i./ha starting with pod initiation at 15 days interval proved to be the most effective treatment against podfly whereas endosulfan applied twice @ 1.050 kg a.i./ha formed the most effective schedule against rest of the insect species.

8. Data on benefit cost ratio indicated the highest ratio (5.19 : 1) to be associated with monocrotophos at lower dose (0.400 kg a.i./ha) sprayed once. The additional return over cost was maximum (Rs. 2491. 91/ha) with monocrotophos @ 0.600 kg a.i./ha sprayed twice. The benefit cost ratio was less than (0.78 : 1) with dimethoate at 0.700 kg a.i./ha sprayed once giving a loss of Rs. 76.17/ha.

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STUDIES ON THE RESIDUES OF ENDOSULFAN IN/ON PADDY

Ranjit Ray Sup : *Dr. Lallan Rai*

The strategy of plant protection has undergone a tremendous change with the introduction of the concept of integrated pest management programme. The era of highly persistent agricultural chemicals are gone. Under these circumstances, the use of endosulfan (6,7,8,9,10,10- Hexa chloro-1,5,5a, 6, 9, 9a-hexahydro-6, 9,-methano-2, 4, 3-benzodioxathiepin-3-oxide), a close relative of cyclodiene insecticides, the most persistent agro-chemical known till date, in plant project is assuming greater importance day by day because of its unique biodegradable properties. Its effective use against a few major rice-crop pests has already been reported and its widespread use in rice crop is anticipated because of the strategic change in the concept of plant protection. As such a comprehensive treatment of the entire crop-insect-insecticide situation was felt essential with special reference to the studies on the residues of endosulfan in/on paddy.

Studies on the residues of endosulfan 35 EC on the rice crop var. Kavery and the field soil during summer and kharif and a field evaluation trial on the efficacy of endo-sulfan during kharif of 1980 were carried out in the research farm and the laboratory of Department of Entomology, Banaras Hindu University, Varanasi, India (25.2°N, 83.0°E; 75.84m altitude).

The residue trial comprised of two schedules, each having 4 applications of endosulfan at fortnightly interval in two different doses, i.e., @ 0.65 kg/ha and 0.97 kg/ha. All the 4 applications of schedule I were conducted before the carheads began to form whereas in schedule II all the four applications were adjusted in such a way that the last application was made after the earheads began to form. As such, the first application for schedule I and II was carried out at 15 and 22 days after transplanting respectively.

In the field evaluation trial, the performance of the endosulfan application schedules was assessed in rice crop along with three other insecticidal treatments, viz., fenitrothion EC, quinalphose EC and carbofuran G, each at 0.65 kg/ha, against stemborers, leaf and plant hoppers and gundhi bugs. Insecticidal deposits/residues on rice crop and the soil were estimated quantitatively by microbioassay (using 1-day *D. melanogaster* Meig. by residue film method; by colorimetric method described by Maitlen *et al.* (1963) and by thin layer chromatography (using $AgNo_3$ impregnated silica gelG plates). Residues of Endosulfan was assayed in the paddy grain (whole as well as dehusked), husk, straw and soil.

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Microbioassay was found to be the most efficient technique with sensitivity and minimum detectable limit ranging in between 0.0017 ppm (field water) and 0.0273 ppm (green plant) and 0.0089 ppm (field water) and 0.1651 ppm (green plant) respectively. Therecovery of endosulfan was higher with the microbioassay possibly because of using uncleaned extract. The response of *D. melanogastcr* to endosulfan was found to differ with different substrate-extracts LD 50 values ranging between 0.4382 ug (straw) and 0.6496 ug (dehusked rice). Consequently, the sensitivity and minimum detectable limits also varied with the substrates. In case of other methods no such variation was observed. The concept of t_{Sen} (time required to dissipate to the level of sensitivity) has been replaced by t_{MDL} (time required to dissipate to the level of minimum detectable limit of the method) in the present studies. The thin layer chromatography kept a track on the alpha and beta isomers of the insecticide during degradation.

There was no appreciable difference between magnitude of initial deposits between the schedules, or between the seasons in the case of plant materials but in case of soil, kharif recorded greater initial deposits in comparison to summer.

In plant materials, rate of dissipation in general was a little higher in kharif in the early days. But the dissipation was much slower during thc first two applications in summer and the last two applications in kharif possibly because of a little or no rainfall during these periods. The half-life values were much variable, ranging from 1.55 day to 3.86 days (6.01 days when the observation of the 28 day was included), consequent upon the vast environmental fluctuations during the entire crop length.

Rainfall on the day of treatment has been identified as the most effective dissipating factor. It did not show any effect when occurred a few days after treatment. Other factors like temperature, relative humidity and sunshine seemed to operate simultaneously. The lower temperature and relative humidity of the atmosphere prevaling during the 4th application in kharif could have been the reason for detection of residues in the 28 day samples.

On the contrary, in soil, the rainfall affected the degradation only when the precipitation was heavy enough causing run-off. Wherever there were rainfall on the day of treatment, the dissipation of endosulfan in soil after one-day of application was found to be slower possibly due to addition of dislodged insecticide from the plant. Initial deposits declined gradually with the subsequent spray inspite of the carryover residues, if

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any, from the previous applications; the gradual growth of the plant canopy probably stood on the way of higher insecticidal deposition in the soil. The considerable gap (almost one-day) between the sampling and the extraction, allowed for air drying of the wet samples, might have been the cause of detecing much lower deposit/residues in the soil.

The ratio of alpha and beta isomers in the initial deposits was little higher with the higher doses. The gap reduced with the process of degradation. The ratio of alpha beta reached around unity after 3-days and was shifted/reversed after 5 days in plant material but the ratio was shifted within 3-days in case of soil.

At harvest, no endosulfan residue was found in grains (whole as well as dehusked), husk, straw and soil during summer. But during kharif, a minute quantity of beta endosulfan was traced in plant material and in soil at both the doses of schedule I, whereas beta endosulfan with traces of alpha isomer in plant materials and beta isomer alone in soil were detected in the schedule II. The higher amount of residues detected in schedule II was because of the lower gap between the last application and harvest. The residues detected in straw were far below the general tolerance limit of 2.0 ppm and hence these are not considered to be harmful to cattle. In kharif, no residual endosulfan was detected in the rice grains, either whole or dehusked. The rice husk also was found to be free from residues.

Endosulfan at 0.97 kg/ha of schedule II was proved to be the best in reducing the pest population and in achieving higher yields (57.30 per cent more over control) followed by the treatment with quinalphos at 0.65 kg/ha. However, there was no significant difference in yield among the endosulfan treatments.

It is concluded that endosulfan dissipates in the rice crop and the soil quite rapidly, leaving residues far below the tolerance limit of 2 ppm. The straw of endosulfan treated crops may safely be fed to cattles as soon as it is harvested. No endosulfan residue was detectable in paddy grain on its husk even when treated with the higher dose at earhead forming stage. Although, there was no significant difference in yield among the endosulfan treatments, the higher dose application of 0.97 kg/ha may be advocated even at earhead forming stage, if at all required, without any apparent ill effect to the consumers or the environment.

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GENETICS & PLANT BREEDING

GENETIC ARCHITECTURE OF YIELD AND YIELD TRAITS IN CHICKPEA (*CICER ARIETINUM L.*)

Amita Agnihotri Sup. *Dr. V. P. Singh*

The present investigation was carried out to determine the nature and magnitude of genetic variation, gene action, combining ability variances and effects, heterosis and inbreeding depression for yield and yield attributing traits in chickpea *(Cicer arietinum* L.) involving *desi* and *kabuli* types by employing diallel and line x tester analyses.

The present study consisted of 17 diverse and elite cultivars of chickpea. Of these, 14 cultivars, namely, BG 203, BG 209, BG 225, GL 769, H 208, ICCC 8, ICCC 9, JG 74, K 468, K 903, K 904, Pant 114, T 3 and T 6 were *desi* and 3 cultivars, *viz.*, JM 482, K 4 and K 13 were *kabuli* types.

The study was accomplished following three different experiments. Experiment I comprised a 10×10 diallel of *desi* chickpea, consisting of 10 parents, 45 F_1s and 45 F_2s which was grown in a randomised block design with three replications. Experiment II included an 11×11 dialled of *desi* and *kabuli* types, consisting of 11 parents and 55 F_1s which was grown in a randomised block design with three replications. Experiment III consisted of a 6×3, line $\times$ tester set of *desi* (lines) and *kabuli* (testers) chickpea including 9 parents, 18 F_1s and 18 F_2s and was grown in a randomised block design with four replications.

The characters studied in Experiment I were plant height, number of primary branches per plant, number of secondary branches per plant, number of pods per plant, number of seeds per pod, grain yield per plant, 100-seed weight and protein content. The characters studied in Experiments II and III were plant height, number of primary branches per plant, number of secondary branches per plant, number of pods per plant, number of seeds per pod, grain yield per plant, 100—seed weight, seed coat percentage, days to 50 per cent flowering, days to 50 per cent fruiting and days to maturity. The data on yield and yield characters were recorded from 10 randomly selected plants for each of the parents and F_1s and from 50 plants for each F_2, excluding the border plants.

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The diallel progenies were subjected to graphical, component and combining ability analyses. The progenies of line × tester matings were subjected to component and combining ability analyses. The heterosis over better parent and mid-parent was estimated in all the three experiments. The inbreeding depression was estimated in Experiment I and Experiment III.

The progenies differed significantly for all the characters in all the three experiments except for number of primary branches in F_2s of Experiment I.

The t^2 estimates were non-significant for plant height, number of secondary branches per plant and protein content (F_1, F_2) and number of seeds per pod (F_1) in Experiment I and for plant height, number of seeds per pod, 100—seed weight, seed coat percentage and days to 50 per cent flowering in Experiment II, indicating the fulfilment of the assumptions of diallel analysis. The significant t^2 values for number of pods per plant and 100—seed weight in F_1 and F_2, number of primary branches per plant in F_1 and number of seeds per pod in F_2 in Experiment I and for number of primary branches per plant, number of secondary branches per plant, number of pods per plant, grain yield per plant, days to 50 per cent flowering and days to maturity in Experiment II, suggested the failure of at least one assumption of the diallel analysis.

The significant deviation of regression coefficient 'b' from unity for all the characters in both the experiments (I and II), except for plant height (F_1, F_2), number of primary branches per plant (F_1) in Experiment I and 100—seed weight and seed coat percentage in Experiment II suggested the presence of epistasis and/or correlated gene distribution among the parents for these characters.

Graphic analysis revealed overdominance for plant height and number of secondary branches per plant in F_1 and F_2 and protein content in F_2 in Experiment I and for number of primary branches per plant, number of pods per plant, grain yield per plant, seed coat percentage and days to 50 per cent flowering in Experiment II. The partial dominance was observed for number of pods per plant and 100—seed weight (F_1, F_2), number of primary branches per plant and protein content (F_1), seeds per pod and grain yield per plant (F_2) in Experiment I and for secondary branches per plant, seeds per pod, 100—seed weight, days to 50 per cent fruiting and days to maturity in Experiment II. However, the complete dominance was revealed for number of seeds per pod and grain yield per plant in F_1 in Experiment I and for plant beight in Experiment II. The Wr, Vr and the standardised deviation graphs showed a linearity in the distribution of parental points for most of the characters.

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The genetic component analysis revealed the significant additive component (D) for plant height, 100—seed weight and protein content (F_1, F_2), number of secondary branches per plant and seeds per pod (F_2) in Experiment I and for number of seeds per pod, 100—seed weight, seed coat percentage, days to 50 per cent flowering, days to 50 per cent fruiting and days to maturity in Experiment II. The dominance components (H_1 and H_2) were significant for all the characters in both Experiments I and II except for number of seeds per pod (F_2) in Experiment I. The 'h^2' was significant for plant height and number of secondary branches per plant (F_1, F_2), number of pods per plant, grain yield per plant and protein content (F_1) in Experiment I and for secondary branches per plant, number of pods per plant, grain yield per plant, seed coat percentage, days to 50 per cent flowering, days to 50 per cent fruiting and days to maturity in Experiment II. In Experiment III, the higher magnitudes of additive genetic variances were observed for grain yield per plant, 100—seed weight, days to 50 per cent flowering, and days to maturity. The higher magnitudes of dominance genetic variance were observed for plant height, number of pods per plant, grain yield per plant, 100—seed weight, seed coat percentage and days to 50 per cent fruiting.

The degree of dominance in all the three experiments showed preponderance of dominance component for all the characters except 100—seed weight in Experiment II and number of primary branches per plant in Experiment III. The ratio $H_2/4H_1$ was close to 0.25 for plant height and number of primary branches per plant in F_1 and number of seeds per pod in F_1 and F_2 in Experiment I and for seed coat percentage in Experiment II, suggesting a symmetrical distribution of genes with positive and negative effects in the parents. The ratio KD/KR was more than one for all the characters except number of primary branches per plant (F_1), number of seeds per pod and 100—seed weight (F_1, F_2) in Experiment I and number of secondary branches per plant in Experiment II, suggesting the presence of an excess of dominant genes among the parents. The ratio h^2/H_2 in Experiment I revealed that one or two genes/groups of genes were present among the parents which exhibited dominance while in Expertment II, it revealed that 1 to 4 genes/groups of genes were present in the parents which exhibited dominance.

Both additive and nonadditive gene effects were important for different characters with a difference in the relative magnitudes of the two.

The mean sum of squares due to gca and sca were significant for all the characters in Experiment I and II except for number of primary branches per plant in Experiment I. In Experiment III,t he variances due to

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gca were significant for number of seeds per pod (F_1, F_2) and number of primary branches per plant and days to 50 per cent flowering (F_1). The variances due to sca were significant for all the characters except number of primary branches per plant and number of seeds per pod.

The ratio $2\,6^2g/6's$ was less than one for most of the characters, except 100—seed weight and protein content (F_1, F_2), seeds per pod (F_1) and grain yield per plant (F_2) in Experiment I and number of seeds per pod and 100—seed weight in Experiment II and number of seeds per pod and 100—seed weight (F_1, F_2), number of primary branches per plant, days to 50 per cent flowering and days to 50 per cent fruiting (F_1), number of secondary branches per plant, and grain yield per plant (F_2) in Experiment III. For plant height and number of pods per plant the ratio was less than one in all the three experiments, thus suggesting a preponderance of nonadditive gene effects for these characters. However, for number of seeds per pod and 100—seed weight, the ratio was more than one in all the three experiments which suggested for the preponderance of additive gene effects for these characters.

The significant gca and sca effects were observed for different characters in all the three experiments. The parent T 3 was a good general combiner for most of the characters. The crosses T 3 × Pant 114 and T 3 × JM 482 were the best specific combiners for many characters. The crosses with high sca effects involved either good × poor, poor × poor or good × good general combiners, The crosses with high sca effects involving good × poor general combiners were of most frequent occurrence.

In general, there was a positive relationship between the gca and sca effects of parents and crosses and their *per se* performance.

A high heterosis over better parent and mid-parent was observed for all the characters in all the three experiments. Both positive and negative significant inbreeding depression were also observed for different characters as estimated in Experiments I and III. The crosses revealing high heterotic effects usually showed significant sca effects although the gca effects of the parents in general were poor. Further, the crosses exhibiting high heterosis usually involved either good × poor, average × poor or poor × poor general combiners revealing the importance of nonadditive effects. The high heterotic values (above 100 per cent) were observed for grain yield per plant, number of secondary branches per plant and number of pods per plant in all the three experiments which suggest for exploitation of heterosis in breeding for chickpea improvement by applying the appropriate breeding techniques either by evolving male sterile lines or by using technique of crossing without emasculation.

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In view of the above findings as revealed by the present investigation and in the light of discussion based on known reports, certain recommendations have been chalked out for improvement of chickpea,

GENETIC STUDIES ON INTERSPECIFIC HYBRIDS IN *CICER*

Hemant Kumar Jaiswal Sup : *Dr. B. D. Singh*

Pulses are the prime source of protein in developing countries like India and they play an important role in combating the protein-calorie malnutrition so widely prevalent in the developing countries. Pulse production has remained stagnant at 11-12 million tonnes for the last two decades. The optimum daily requirement of pulse per capita is 104 gms but only 43.8 gms is available. An increase of 8-10 million tonnes of pulses is necessary to fulfil the needs of the consumers. In order to arrest and reverse this trend, it is imperative to increase the production as well as the quality of pulses to combat protein malnutrition.

Gram (*Cicer arietinum* L.) is the foremost pulse crop of India For some time to come, improvement of gram will depend on intraspecific or intervarietal hybridization. But the progress in improvement has been slow and it may be worthwhile to explore the related wild species as possible donors of genes for yield improvement and resistance to diseases and pests.

Three wild species viz., *C. reticulatum*, *C. judaicum*, and *C. cuneatum* were chosen and crossed with *C. arietinum*. Only *C. reticulatum* readily hybridized with *C. arietinum*. Per cent success in crossing was 5-9 per cent in the crosses between *C. arietinum* and *C. reticulatum*. Empty pods were obtained when *C. arietinum* was used as female in crossing with *C. judaicum* and *C. cuneatum*. Two genotypes, one *desi* cv. T 3 and one *kabuli* ICC 8923 of *C. arietinum* were crossed with *C. reticulatum* JM 2106 in both ways. F_1, F_2, B_1 and B_2 of the four crosses along with the two parents were grown in a randomized block design with three replications. Data were recorded on leaflets/leaf, leaf length, leaflet length, plant height, primary branches, secondary branches, pods/plant, pod length, seeds/pod, yield/plant, 100-seed weight, days to flower and days to maturity. In case of the parents and F_1, 10 random plants were selected for observation from each plot while in each F_2 100 plants and in B_1 and B_2 20 plants were selected. Frequency distribution graphs of F_2 were prepared for various characters under study to examine variability patterns, and to assess if there was

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any evidence for zygotic elimination. Using the six generations from the four crosses, gene effects were estimated by employing generation means analysis devised by Mather (1949) and Jinks and Jones (1958). The A, B and C scaling tests, Mather (1949) and the Joint Scaling Test attributed to Cavalli (1952) were performed to detect the presence of epistasis.

Desirable segregants in F_2 were selected from the four crosses. Heritability by parent-offspring regression (Robinson *et al.* 1949) was estimated for eight agronomic characters in the selected F_2 plants. Character associations were calculated in the selected F_2 plants and their respective F_3 progenies, crosswise.

The pollen fertility (per cent stainable pollen) in F_1s between *C. arietinum* and *C. reticulatum* was normal and comparable to that of the parents. Frequancy distribution in F_2 was generally unimodal and there was transgressive segregation for all the characters. This indicates that there was no selective zygotic elimination in F_2. Absence of pollen stainability shows that there was no selective genetic elimination in F_1.

Analysis of variance for 13 yield and yield traits showed significant differences among the six populations for most of the cases in the four crosses. The joint scaling test proved more powerful in identifying the presence of epistasis. Out of 44 tests performed, 40 times the joint scaling test proved correct. The results of the joint scaling test were confirmed by the significance of i, j, and l estimates from the six parameter model. In the four cases of disagreement the joint scaling test showed epistasis while the estimates of i, j and l were nonsignificant. This indicates that the joint scaling test has a tendency of overestimating epistasis.

The noninteracting crosses were subjected to the three-parameter model to study gene effects, while the six-parameter model was used for estimating the gene effects in the interacting crosses. Most of the characters were governed by additive gene effects; for secondary branches and pods/plant both dominance and (i) interaction seemed important. Seeds/pod recorded both additive and dominance gene effects. Pod length, yield/plant and 100-seed weight seemed to be under control of additive gene effetcs with some dominance and interaction effects. Days to flower showed all the types of gene effects and interactions, while days to maturity recorded additive gene effects only.

Heterosis manifestation was negligible in spite of the greater contribution of interaction gene effects. Negative heterosis was evidenced for most of the crosses studied, except secondary branches, pods/plant, days to flower and days to maturity. Inbreeding depression was recorded for most of the

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characters and it ranged from 0.15% for leaf length to 54.71% for pods/plant. No heterosis was recorded for leaf length, leaflet length and 100-seed weight in any of the crosses.

A variable number of plants were selected from each of the four F_2 populations on the basis of five yield and yield traits viz., plant height, secondary branches, pods/plant, yield/plant and 100-seed weight. A total of 238 single plant progenies were grown in F_3 along with the parents in a randomized block design with two replications. In general, the heritability estimates from parent-offspring regression were low, except for plant height and 100-seed weight. Realized genetic advance in F_3 and expected genetic gain in F_4 was moderate for plant height and 100-seed weight. Genetic gain in F_4 was low and showed rather poor improvement for secondary branches and pods/plant.

Among the selected lines, several showed improved yield traits than either of the parents. Cross ICC 8923 x JM 2106 gave a very large variability for all the characters and a number of lines were selected for F_4 evaluation on the basis of certain yield attributes.

Four plants selected in F_2 for early flowering (37-42 days) produced homogeneous F_4 progenies for early flowering. Out of these, line 250-1 showed cold tolerance in flowering and pod setting. This line set pods between 15th December to 10th January when night temperatures were as low as 5-7° C. It had small leaves, pods and seeds. These lines are being used in crossing programmes as sources of earliness and cold tolerance.

Correlation coefficients were estimated in selected F_2 plants and their respective F_3 progenies separately for the four crosses. Yield/plant showed significant positive correlation with secondary branches, pods/plant and seeds/pod, whereas its association was negative with habit and significantly negative with plant height and 100-seed weight in F_2. In F_3, cross ICC 8923 x JM 2106 recorded significant positive correlation between yield/plant and plant height.

There were five cases of reciprocal differences in the F_1 generation from crosses between *C. arietinum* and *C. reticulatum*, but these differences persisted only in the case of plant height in the F_2 generation of one cross. *C. reticulatum* cytoplasm tended to reduce the spread of frequency distribution curves for most of the characters in the crosses having *C. reticulatum* as female. Similarly, a lower number of significant gene effects and character associations were recorded in crosses having *C. reticulatum* as female parent. It appears that *C. reticulatum* cytoplasm was detrimental to recovery of transgressive segregants and adversely affected character associations. Thus, using *C. reticulatum* as female parent in crossing should be avoided.

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From the cross ICC 8923xJM 2106 and its reciprocal a number of F_3 and F_4 lines were isolated that had seed characters of the *desi* type chickpeas; these lines also had plant type comparable to the *desi* cultivars. This indicates that some *desi* type chickpeas could have arisen as a result of introgression of genes from *C. reticulatum* into *kabuli* type *C. arietinum*.

A number of undesirable characters of *C. reticulatum* tended to reduce the value of the selected lines. Hard reticulate seed coat and dark seed colour affected the quality of the grain. Prostrate or semiprostrate plant habit is agronomically uudesirable as the plants tended to interlock with one another and many pods were lost due to snagging at the time of harvest. Pot shattering at maturity also affected the yield adversely in a number of lines. A few lines which were otherwise good performers had to be rejected due to phenolic bitter taste of seeds. An effort has to be made to avoid these characters while selecting in the segregating generations of crosses having *C. reticulatum* as one of the parents.

Based on the findings of this study, it may be concluded that introgression of *C. reticulatum* genes into *C. arietinum* is likely to improve the yield and yield traits of the latter. Selection for yield and yield traits in F_2 was ineffective, and backcrossing would be tedious and may be expected to reduce the population size. and thereby the chances of recovery of transgressive segregants. It is suggested that selection should be made on F_3 or F_4 individual plant progenies. The selected progenies may then be backcrossed to *C. arietinum* once or twice and the segregating generations subjected to pedigree method of breeding with the modification that selection should be done in F_3 or F_4 to overcome the low heritability of yield traits in early generations. It would be desirable to use an outstanding *kabuli* or *desi* type of *C. arietinum* in hybridization with *C. reticulatum* in order to further assess the usefulness of introgression of *C. reticulatum* genes in chickpea improvement.

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CYTOGENETIC STUDIES ON INDUCED AUTOTETRAPLOIDS AND CERTAIN ANEUPLOIDS IN PEA *(PISUM SATIVUM L.)*

Mercy Kutty V. C. Sup. *Dr. Hriday Kumar*

Four diverse cultivars of pea (*Pisum sativum* L., 2n = 14), namely, T 163 (indigenous), 68C, 5064-S and PI280064 (all the three exotic) were chosen for the induction and characterisation of autotetraploids and their subsequent exploitation in the production of aneuploids. Using aqueous solution of colchicine (0.025, 0.05, 0.10 and 0.15%), 1.5-2.0 cm long seedlings were treated for 4 and 8 hr, whereas 12 hr presoaked seeds were treated with 0.025 per cent solution for 1, 2, 4 and 8 hr and planted in the field.

Treatment of seedling (4 hr) and seed (1 and 2 hr) with 0.025 per cent colchicine was most efficient yielding about 9.0 and 5.0 per cent viable autotetraploids, respectively. High mortality right from germination to harvesting was noted in seed than seedling treatment. Large seeded cultivars were more responsive to treatment than the small ones.

Autotetraploid showed slow but vigorous growth with dark green, thick and large stipules and leaflets. It differed significantly from diploid in having large stomata, flowers, pollen grains, seeds and delayed flowering and maturity by 15-20 days, while stomata frequency and pod length showed reduction; the magnitude of increase or decrease was noted to be genotype specific. Cytologically autotetraploid was characterised by the presence of doubled chromosome number and varying frequencies of quadrivalent and bivalent, among others.

Autotetraploids in C_1, C_2 and C_3 generations and materials relating to experiments on selection, mutation and hybridization were harvested as per the requirements.

Data on chromosome configurations at MI, disjunction index (D. I.), AI anomalies, pollen sterility and number of seeds per pod were analysed from C_1, C_2 and C_3 generations of autotetraploids. Chromosome behaviour at MI and AI and D.I. varied significantly with the cultivar and generation. A positive shift from C_1 to C_3 in mean bivalent at the cost of quadrivalent in autotetraploids of all the cultivars was noted. Decline in AI abnormalities from C_1 to C_3 generation was associated with increase in D. I.

Data on chromosome configurations at MI and AI from parents, F_1 and F_2 progenies of a 4×4 diallel cross involving tetraploids were analysed. Since chromosome configurations did not significantly vary due to two dates of PMCs collections, average values regarding them were considered.

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F_1 recorded a decline in quadrivalent frequency compared to the parents at the cost of bivalent. As compared to F_2, crosses T163 × 68C and T163 × PI280064 in F_1 showed significant decrease in quadrivalent and increase in bivalent frequency.

Significant differences in pollen sterility (only due to generation) and seed set in autotetraploids due to cultivar and generation were noted. 'Treated diploids' in C_1 generation also showed fairly high magnitude of pollen and seed sterility, but had no chromosome abnormality at AI. Autotetraploid of the cultivars, T163 and 5064-S showed significantly higher seed set than the others.

Pollen fertility in induced autotetraploids ranged from 21 to 70 (modal class, 41-50) and 41 to 90 (modal class, 71-80) per cent in C_1 and C_2 generations, respectively. Cell with 1-2 univalents and one trivalent were most frequent.

A few diploid plants in the progenies of induced autotetraploids were noted; frequency was more in C_1 progenies as well as in whole plant bulk harvesting than those in C_2 progenies and in branch-wise harvesting, irrespective of the cultivars.

Chiasma frequency was scored considering the varied appearance of chromosome configurations at MI following Ward (1976), which permitted partitioning of the total chiasmata into proximal (P) and distal (D). In autotetraploid, chiasma frequency scored by the revised method was relatively higher than those scored by the conventional method. Revised method of chiasma scoring hold great promise not only because of its greater precision in chiasma scoring but also in locating the positional distribution of the chiasmata.

Variances due to cultivar and generation were highly significant for proximal and total chiasmata. Both proximal and total chiasmata recorded positive shift from C_1 to C_3 generation. Autotetraploid of the cultivar 5064-S recorded maximum chiasmata.

Chiasmata formation in progenies derived from 4 × 4 diallel crosses among tetraploids and diploids were studied from PMCs collected on two dates (D_1 and D_2 at the interval of 20 days), first collection coincided with the 50 per cent flowering. Progenies differed significantly for proximal, distal and total chiasmata; variances due to date, genotype and their interactions were significant for all the three estimates except proximal, for which interaction was insignificant.

Mean proximal and distal chiasmata per cell markedly increased at both the ploidy levels as compared to parents in both F_1 and F_2 generati-

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ons. At tetraploid level, total chiasmata in F_1 were maximum in cross T-163 × 68C (41.80 in D_1; 38.70 in D_2). Chiasmata formation in parental autotetraploids showed significant decline (except 5064-S) as compared to their respective diploids (2x.2), while most of the crosses showed increase in total chiasmata (increase reflected in both proximal and distal chiasmata) in tetraploid in both F_1 and F_2 as compared to diploid, though varied with genotype. Averaged over two dates of chiasma scorings, F_2 generation recorded a gradual decline in chiasma fequencies, particularly of distal and total in autotetraploid in relation to diploid.

Different dates of PMCs collection (D_1 and D_2) had more effect on distal than proximal chiasmata. On an average, D_1 recorded more chiasmata formation by about 5.50 to 12.70 per cent over the D_2; reduction in D_2 was more in the parent 68C at both the ploidy levels.

Heterosis in crosses with regard to chiasma frequency was more or less parallel in two dates of chiasma scorings and was significantly high in tetraploid than diploid, while reverse was true for inbreeding dipression.

Chromosome doubling had markedly reduced the pollen and seed fertility. With a view to improving the fertility of autotetraploids (seed production), three breeding procedures, such as, selection, mutation and hybridization were exploited in the present case. Pollen fertility, as judged from stainability of Pollen grains with iodine solution, showed no relationship with seed set in both C_1 and C_2 generations, and hence, could not form the basis of selection for fertility improvement in autotetraploids.

Four seed set groups of plants *viz.*, unselected 'general' and selected 'high', 'medium' and 'low' were studied in each of the 3 generations of autotetraploids of two cultivars, T 163 and 5064-S. These groups were constituted in C_1 generation out of 10 randomly selected autotetraploids. Each group had seeds of two plants having more or less similar level of D. I. as well as seed set. In C_2 generation, 10 plants were selected randomly in each of the four groups. Two seeds each from 10 randomly selected autotetraploids were drawn and bulked to make 20 seeds in each of the four groups to raise C_3 generation. Data on chromosome configurations, disjunction index, chiasmata formation per cell, and seed set were analysed.

Selection resulted a gradual shift in seed set, though the magnitude and nature of shift varied with the group and generation. On an average, improvement in the seed set from C_1 to C_3 generation was associated with decline in quadrivalent and increase in bivalent, D. I. and total chiasmata. 'Low' seed set group recorded no appreciable change in the quadrivalent frequency as compared to unselected 'general' group. High frequency of

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bivalent per cell was noted in 'high' seed set group compared to others. D. I. and total chiasmata recorded gradual improvement from C_1 to C_3 generation in both the cultivars. In both the cultivars, 'high' seed set group had high D. I. compared to others. Increase in total chiasmata was mostly due to an increase in proximal chiasma.

With a view to exploiting the induced mutation in improving the fertility, seeds of autotetraploids and their corresponding diploids of all the four cultivars were irradiated with 10 Kr gamma-ray. In general, autotetraploids were more sensitive than their corresponding diploids, as judged from germination, survival and chromosomal damage in root tip cells. AI abnormalities, pollen and seed sterility in autotetraploids did not differ significantly from their corresponding controls, while in diploids, a significant increase in pollen and seed sterility was noted.

In M_2 generation, seed samples from the selected M_1 plants having seed sterility less than 20 and 55 per cent, respectively in diploids and autotetraploids of the two cultivars, T163 and 5064-S were bulked treatment-wise and sown in RBD with 3 replications. Bulked seed samples from the M_1 plants belonging to T163 and 5064-S, which were used for cytological studies, were raised separately for cytological studies. In M_2/C_3 generation of autotetraploids, a significant increase in bivalent coupled with a reduction in univalent frequency and AI abnormalities were noted as compared to M_1/C_2.

In M_2 generation, ANOVA for certain economic traits, such as, number of pods per plant, pod length, number of seeds per pod, 25-seed weight and seed yield per plant revealed that variances due to cultivar, ploidy and their interactions were highly significant for all the traits except number of pods per plant and seed yield per plant, where cultivar effect was insignificant. Treatment means decreased from their respective controls. But a positive shift for number of seeds per pod, though insignificant, in autotetraploids of both the cultivars was noted. In both the cultivars, number of pods per plant and seed yield per plant recorded high variation (about 1.5 to 3 times) in M_2 generation; variation was relatively more in the autotetraploids.

A few M_2 plants having seed yield higher than the respective diploid controls were isolated from the treated diploid and tetraploid populations. Promising M_2 plants (%) were 13.33 and 11.67 in diploid and 11.25 and 6.67 in autotetraploid, respectively in the cultivars 5064-S and T 163.

Data on plant height, number of pods per plant, pod length, number of seeds per pod, 25-seed weight, seed yield per plant, total protein content

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and chiasmata formation were recorded from parents, F_1 and F_2 progenies derived from 4×4 diallel crosses at tetraploid and diploid levels separately and statistically analysed. For all the characters the variances for each comparisons were highly significant.

Magnitude of heterosis was remarkably high in tetraploids as compared to diploid, particularly for number of pods per plant, number of seeds per pod and seed yield per plant.

A significant increase in total protein content was recorded in autotetraploids as compared to respective diploids; the magnitude of increase in autotetraploids (as per cent of their corresponding diploids) ranged from 6.55 (5064-S) to 19.54 (PI280064). At both the ploidy levels, protein content showed negative correlation with seed index.

Data on hybridization revealed the superiority of the cross T163 × 68C at both the ploidy levels compared to others as it showed, on an average, a positive interaction for seed yield and protein yield per plant and chiasmata formation.

In autotetraploids, among the three breeding procedures *viz.*, selection mutation and hybridization in relation to fertility improvement, hybridization followed by selection in segregating generation (F_2/C_3) was most efficient. This procedure had released recombinants with high seed yield at par/even better than the diploid T163 coupled with high protein content.

All the morphologically distinct tetraploids in C_2, C_3 and F_2/C_3 (derived from 4×4 diallel cross) generations were subjected to cytomorphological studies. There was a predominance of hyperploids compared to hypoploids. F_2/C_3 generation had about 2.5 times more aneuploids than C_2 and C_3 generations.

Seven types of trisomic tetraploids ($4n - 1 = 27$) were scored, which were characterised by the presence of stipule and leaflets with thin blade along with their altered shape. The leaflets were large and round, round, large, compactly arranged, clustered, small and reduced. AI anomalies and pollen fertility were high.

Six types of pentasomic tetraploids ($4n + 1 = 29$) were isolated which were characterised by the presence of a very close and compact arrangement of stipule and leaflets. Leaflets were large, round, normal, round, small and round and very large. Pentasomic tetraploids were characterised by the presence of a pentavalent at MI.

Three types of hexasomic tetraploids ($4n + 2 = 30$), one double pentasomic tetraploid ($4n + 1 + 1 = 30$), one multiple aneuploid tetraploid

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($4n+2+1+1\times1=33$) were also isolated. Plants with 30 chromosomes were morphologically very distinct from the control and had semi-dwarf to dwarf plant height. At MI, hexasomic tetraploid was characterised by the presence of a hexavalent and high frequency of cells with 7IV + 1II association, while double pentasomic tetraploid showed presence of 2V + 5II association. Multiple aneuploid tetraploid was characterised by its very vigorous growth with highly increased size of leaflets and stipule and had varying frequencies of hexavalent and pentavalent. AI anomalies were very high.

Crosses between autotetraploid and diploid were attempted. In $4\times(♀)\times2\times(♂)$ crosses, a few pods developed but without any normal seed (only a few plumpy grains). While in reciprocal crosses, F_1 pod formation was relatively more and had 1.48 seeds per pod. None of the F_1 seeds were triploid.

Twenty two (0.883 %) numerical aberrants were isolated from the mutagen treated (F_2/M_2 and F_3/M_3) and normal diploid populations; they were more frequent in the treated populations. Out of these, tertiary and interchange trisomics amounted to five and nine, respectively. Other numerical aberrants were tertiary trisomic interchange heterozygote (1), primary trisomic (2), double trisomic (2), mutant with 13 chromosomes (1), tetrasomy (1), and quadriple trisomy (1).

Tertiary and interchange trisomics were distinguishable by their poor vigour, thin stem, narrow stipule and leaflets. Five tertiary trisomics were put to four groups, whereas all the nine interchange trisomics were morphologically distinct from each other. In tertiary trisomics the modal chromosome configuration was 1III + 6II. While in interchange trisomics, characteristic configurations were 10_4 + 5II + 1I and 1III + 6II. Per cent pollen fertility and 7-8 disjunction were about 45.00 and 66.67 in tertiary trisomics and 57.00 and 71.00 in interchange trisomics, respectively. Seed yield was poor and ranged from 0 to 4 seeds per plant.

A tertiary trisomic interchange heterozygote (L37-1) in F_2/M_2 generation was isolated; it was characterised by the presence of weak and slender stem, profuse semi-spreading branches, narrow stipule and leaflets. This mutant had high pollen and ovule sterility (76-88%). At MI, chromosome configuration 5II+2II (heteromorphic)+1I (small chromosome) was observed in 85 per cent cells.

Primary as well as double trisomics were distinguishable morphophysiologically from sister diploids and from one another, characteristic feature being leaflets morphology. In primary trisomics, the modal chromosome association at MI was 7II+ 1I. Plants with 16 chromosomes

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showed configuration of 2III+5II in 50-60 per cent cells. Pollen and seed sterility and AI abnormalities were relatively more in double than primary trisomics.

One off-type plant in the progeny of translocation heterozygote showed extreme degree of reduction of all plant parts and it did not reach to its flowering stage. The leafsheath somatic chromosome analysis of the mutant, using the modified squash technique developed during the course of investigation, indicated the presence of 13 chromosomes per cell.

Tetrasomy and quadriple trisomy were morphologically distinguishable from each other and from the respective sister diploids and had high pollen sterility. In tetrasomy the chromosome configuration 1IV + 6II was most frequent, while in quadriple trisomy cells with 4III+3II was predominant.

Two mutants, morphologically alike, with high pollen sterility and 14 days late flowering compared to their diploid sibs were isolated. They were characterised by the presence of one small bivalent at MI and multiple interchanges involving 5 to 11 chromosomes. AI indicated the presence of 15 chromosomes per cell.

Four off-type plants with 14 chromosomes were isolated; among these, 3 plants were morphologically similar to sister diploids, but flowered earlier by 10 days. At MI, chromosome configurations of 1IV + 5II and 7II (with the presecne of two contrasting sizes of bivalents—one was larger than the other, in every cell) were observed. Normal disjunction of both the bivalents at AI was noted in 70 per cent of cells. Other plant was morphologically almost similar to its respective euploid but flowered 18 days late and had high pollen sterility. At MI, chromosomes association of 1VI+4II, 2III+4II and 1IV + 5II were in varying frequencies.

One off-type plant with 27 chromosomes had 85 per cent pollen sterility, was characterised morphologically. Characteristic chromosome configuration at MI was 1VII+5IV. At AI, besides laggards, a few cells with 1 bridge, 1 fragment, bridge and fragment together were also observed.

Triploid (3n=21) and hypertriploid (3n+1=22), one each, were isolated in M_3/F_3 generation. Triploid was dwarf with hardy stem, larger stipule and leaflets and had flowered early by 9 days but matured late by 10 days compared to its diploid sib. Stomata, flower and seed sizes were intermediate to those recorded in autotetraploid and diploid. Pollen grains were of triangular shape and had 50.50 per cent fertility. Hypertriploid was semi-dwarf but vigorous than the corresponding diploid sibs and characterised by the presence of hardy stem with reduced internode, large size of stipule and leaflets and 10 days early flowering compared to its

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diploid sib. Pollen fertility was 22.76 per cent. None of the direct and reciprocal crosses (between triploid and diploid) produced seed.

In triploid, cells with 7III were most frequent at MI followed by 6III + 1II + 1I. At AI 10-11 disjunction was observed in 26.70 per cent cells. In hypertriploid at MI cells with 1IV + 6III was observed in 15 per cent cells; modal configuration was 1IV + 4III + 2II + 2I.

STUDIES ON INDUCED INTERCHANGES AND QUANTITATIVE VARIATION IN PEA (*PISUM SATIVUM L.*)

Neena Nigam Sup. *Dr. Hriday Kumar*

The present study was undertaken to induce and characterize chromosomal interchanges, to assess the nature and the magnitude of induced variability in M_2 and M_3 generations and the efficiency of the treatments in terms of relationship of M_1 injury/lethality and chromosomal interchanges, chlorophyll mutations and positive micromutations.

Dry seeds of two diverse cultivars of pea (*Pisum sativum* L.; 2n = 14), namely, PI 280064 and T 163 were treated with two doses/concentrations (close to LD_{50}) of gamma-ray (10, 15 Kr), diethylsu'phate (dES; 0.5 and 1.0%) and ethylmethanesulphonate (EMS; 0.1 and 0.2%) under recommended optimal conditions. For chemical treatments, seeds were presoaked with water for 4 hr at 4 ± 1°C and full seeds were maintained at room temperature (28-30°C). Duration of G_1, S and G_2 stages were taken approximately as 3, 4 and 3 hr, respectively on the basis of 10-12 hr duration of total mitotic cell cycle at room temperature (28-30°C). Presoaked full seeds were treated at room temperature with chemicals from 4.45-6.15, 8.00-10.00 and 11.45-13.15 hr after the time of presoaking, respectively failing in middle of their respective G_1, S and G_2 stages. The treatment durations were 1½ hr for G_1 and G_2 and 2 hr for S stage. The seeds were treated with dES at G_1 and S stages and EMS (plus 10^{-6} M $CuSO_4$) at S and G_2 stages. The pH of the treatment solutions were maintained as 7.0 and 7.8 for dES and EMS, respectively using phosphate buffer. The treatment solution of dES was renewed every after 30 minutes.

The controls were carried forward along with the mutagen treatment and were designated as CT-I (with distilled water to serve as a common check), CT-II, III (with phosphate buffer pH 7.0 at G_1 and S stages,

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respectively), and CT-IV, V (with phosphate buffer pH 7.8 plus $CuSO_4$ 10^{-6}M at S and G_2 stages, respectively) served along with the chemical mutagen treatments.

The treated seeds after one hr of washing were sown in laboratory (in saw dust for root tip collection) as well as in field (in completely randomized design). In laboratory, root tips were collected after 48 hr of sowing in acetic : alcohol (1 : 3) and germination was recorded on 7th day. In field, data on germination and seedling height were recorded on 15th and 30th day after sowing, respectively. Plant survival at maturity was calculated against treated seeds sown. Pollen sterility was checked by using 2% iodine solution, and while seed sterility was estimated by counting the total number of scars and total number of well developed seeds per pod.

M_1 plants having more than 10% pollen sterility were subjected to PMC's analysis using usual cytological procedure. Interchange heterozygote plants were isolated and harvested individually. Fertile M_1 plants, having more than 90 per cent pollen fertility, were also harvested individually.

In M_2 generation, fertile plants occurring in the progeny of a interchange heterozygote were crossed with interchange tester stocks and isolation of interchange homozygote and the identification of interchanged chromosomes were carried out during subsequent generations. Further, to identify the chromosomes and their arms involved in inter-changes, 37 interchanges along with their respective controls were subjected to karyotypic analyses from root tip chromo-somes. Both the standard lines, PI 280064 and T 163 were standardised karyotypically in relation to the L 110, a line representing standard normal karyotype of *Pisum*.

Thirteen interchange homozygotes and their corresponding heterozygotes along with treated normals of the cultivar T163 were analysed in relation to plant height (cm.), number of seeds per pod, seed yield per plant (g), 25-seed weight (g), chiasma frequency and seed protein content (%).

The effects of the mutagenic treatments on induced variability were assessed in the M. through M_3 on the basis of range, mean and variances. For this purpose, fertile M_1 plants were harvested separately and 6 groups were made on the basis of pod size. Each of the first three groups had 20 and 30 plants, while rest three had 60 and 90 plants each in PI 280064 and T163, respectively. Seeds were sown in two replications in randomized block design in both the generations. For micromutational studies,

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treatments with gamma-ray and dES with only one control (CT-I) in both the cultivars were considered. The observations on plant height (cm), number of pods per plant, length of pod (cm), number of seeds per pod, seeds yield per plant (g) and 25-seed weight (g) were recorded on randomly selected plants. The number of sampled plants were 10 and 15 in each of the first three groups, whereas 30 and 45 in latter three groups in each replication.

The treatment effects, as judged from the inhibition in germination, survival, seedling height and fertility were significant and showed a good relationship among themselves, though varied with the mutagen and genotype. T163 was more sensitive to all the three mutagens than PI280064 as evident from germination, survival and seedling height. The resistance in PI280064 was more pronounced in chemical treatment than gamma-ray. Treatment at S stage with dES and G_2 stage with EMS were found to be more effective in cultivar T163, while in cultivar PI 280064 treatment at different stages did not produce any significant effect except a decrease in the seedling height at G_2 stage after EMS treatment.

Neither pollen nor seed sterility along appeared to be a reliable measure of radiosensitivity. The cultivar PI280064, assessed to be resistant on the basis of germination, survival and seedling height after EMS treatment, had high pollen sterility (43-64%) parallel to one observed in the sensitive cultivar T163.

Cytological abnormalities in mitotic as well as meiotic cells also suggested higher sensitivity of the cultivar T163 than PI280064. In root tip cells frequent chromosome abnormalities, amongst others, were chromosome breaks, stickiness, clumping, while PMC's showed in addition to breaks, multivalent formation, non-disjunction at Anaphase I and II and multipolar separation. The chromosome breaks in root tip cells were about 2-4 times more than in meiotic cells after gamma-ray treatment in both the cultivars while in chemical treatment they were parallel in the cultivar T163. The cultivar PI280064 had a few chromosome breaks in meiotic cells.

Cultivar T163 recorded relatively more frequency of Anaphase I abnormalities (10.72) than the PI280064 (9.44); dES produced more Anaphase I abnormalities (10.68%) than the EMS (8.61%) in both the cultivars.

The frequency of chlorophyll mutations was calculated on the basis of number of mutants per 1000 M_2 seedlings in each treatment. The fre-

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quency (ten types of chlorophyll mutants such as : *albina*, *costata*, *variegata*, *chlorina*, *chlorotica*, *vario-maculata*, *xantha*, *viridis*, *marginata* and *terminalis*) and spectrum of chlorophyll mutations varied with the mutagen; no cultivar effect was noted. The maximal number of chlorophyll mutations with the broadest spectrum was obtained after treatment with gamma-ray followed by dES and EMS. The frequency of chlorophyll mutations increased with the increase in the concentration of dES, while no such relationship was observed with EMS and gamma-ray treatments. Mutagen specificity with regard to chlorophyll mutations was noted; gamma-ray produced *vario-maculata* 3.53 (times) more than the chemical mutagens and vice-versa was true for *chlorotica*.

None of above mentioned parameters revealed any effect of phosphate buffer alone in both the cultivars.

A total of 61 interchange heterozygotes were isolated in M_1 generation in physical and chemical mutagens treated populations of PI280064 and T163. Induction of interchanges was more in T163 (50) than PI280064 (11). Of the 50 interchanges in T163, chemical mutagens accounted 30 and physical mutagen produced only 20, while in PI280064 gamma-ray produced 10 and chemical mutagens induced only one. Thirty six and ten interchanges out of fifty and eleven survived, respectively in T163 and PI280064 survival being 70 per cent.

The pollen sterility of interchange heterozygotes ranged from 42-99 with an average of 67.16 per cent. On an average, gamma-ray, dES and EMS accounted 58, 66 and 64 per cent pollen sterility. Pollen sterility in interchange heterozygotes in M_1 generation was relatively low in PI280064 (51.28%) than in T163 (62.65%). In M_2 generation, interchanges showed a differential decline in pollen sterility, which was comparatively more in chemical mutagen treatment. In PI280064 interchanges induced at 10 Kr gamma-ray showed high reduction in pollen sterility from about 50 (M_1) to 27 (M_2) per cent.

Ring configurations were in excess as compared to chains in most of the interchanges. Both ring and chain quadrivalents showed a preponderance of adjacent I orientation as compared to alternate. Chromosome configurations and orientations did not vary with cultivar. Variation due to mutagens was statistically insignificant in most of the cases except gamma-ray vs. dES (for pollen sterility in M_1), dES vs. EMS (for cells with 7 II and 5II + 10_4).

The multiple interchange heterozygotes involved upto 4 pairs of chromosomes. Total multiple interchanges induced were 21; 19 in T163

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and 2 in PI280064. Gamma-ray induced 15 multiple interchanges, 13 in T163 and 2 in PI280064, while dES produced 6 only in T163, EMS induced none. Multiple interchanges showed pollen sterilitiy ranging from 41-100 per cent; 67 per cent of them survived. Most of the multiple interchanges with hexavalent (9) had ring configurations, while (2) had only chains. In dES treatment, it was interesting to note relatively low pollen sterility in multiple (56.14%) than the simple (66.45%) in M_1 generation as against the expected 75 per cent.

Most effective treatment was also most efficient in both the cultivars, irrespective of the mutagens. Treatment 15 Kr gamma-ray, 0.5% dES at S stage and 0.1% EMS at G_2 stage were highly effective as well as efficient in producing interchanges in their respective groups.

Based on pollen sterility and chromosome configurations of the F_1 plants (crosses between fully fertile M_2 plants with interchange tester stocks), a total of 40 interchange homozygotes—ten in PI280064 and 30 in T163 were isolated. Both the interchanged chromosomes were identified in 37 interchanges, while only one could be identified in interchanges L-16, L-17 and L-39. All the interchanges except six (L-16, L-17, L-30, L-34, L-38, and L-39) were further analysed karyotypically by comparing the relative chromosome length (L%) ane arm ratio (Pa-value) with that of the standard line to detect the interchanged arm. The results obtained through analysis of F_1 (interchange homozygote x interchange testers) and karyotype of interchange homozygotes regarding identification of interchanged chromosomes were parallel.

The 37 interchanges involved the following chromosome association (values in parentheses relate interchange frequency) : $T_{1-2}(1)$, $T_{1-4}(1)$, $T_{1-5}(4)$, $T_{1-7}(4)$, $T_{2-3}(5)$, $T_{2-4}(1)$, $T_{2-5}(4)$, $T_{2-6}(1)$, $T_{2-7}(1)$, $T_{3-4}(2)$, $T_{3-5}(3)$, $T_{4-5}(3)$, $T_{4-7}(2)$, $T_{5-6}(2)$, $T_{5-7}(2)$ and $T_{6-7}(1)$; remarkably interchanges for T_{1-3}, T_{1-6}, T_{3-6}, T_{3-7} and T_{4-6} were not observed. Random association of different chromosomes leading to formation of interchanges was noted. However, though insignificant, interchanges between chromosome $1-7$ and $2-3$ were found to be 4 and 5 as against their expected values of 1.351 and 1.756, respectively.

Overall, observed breaks were found to be roughly proportional to the chromosome length, as judged from nonsignificance of χ^2_c value. However, chromosomes 2, 5 and 6 did show certain deviations in observed breaks from the expected. The ratio between observed and expected breaks was about 1.5 for chromosomes 2 and 5, while chromosome 6 registered a decline in observed breaks.

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Chromosome breaks were randomly distributed on the two arms in all the chromosomes except chromosome 6. Excess of observed breaks in chromosome 2 were found to be equally distributed on long and short arms, while short arm of chromosome 5 showed accumulation of observed breaks as against expected. No chromosome breaks were found on the long arm of chromosome 6.

Thirteen interchanges were morphologically characterised. On an average, interchange homozygotes, their corresponding heterozygotes and treated normals and controls varied significantly among themselves for most of the traits except number of pods per plant (but interchange homozygote vs. control) and proximal chiasma. Certain interchange homozygotes, namely, L – 21 (T_{2-3}) and L – 55 (T_{2-5}) had significantly high seed yield per plant (18.55 and 17.45 g) as well as protein content (31 – 39 and 30.58%), respectively, against the control (seed yield per plant 13.25 g and protein content 25.48%). Distal chiasma 1.6 times more than the proximal.

Measure of central tendency and variation were estimated in both the M_2 and M_3 generations. The overall analysis of variance showed highly significant differences between the treatments for all the traits in both the generations. Data on each of the six traits were classified group—and mutagenwise and subjected to analysis of variance separately in both the generations. Mean sum of squares due to group in each mutagen treatment and mutagen treatment in each group were significant for most of the comparisons in different traits.

Treatments produced mostly negative effects, as judged from shift in means for all the six traits except in most of the teatments of length of pod and number of seeds per pod. As regards mutagens, dES produced relatively more variability, as judged from coefficient of variation for plant height, number of pods per plant and seed yield per plant as compared to gamma-ray, while both gamma-ray and dES were more or less equally effective for the other three traits. Treatments with 10 Kr gamma-ray and 1.0% dES at S stage were more effective. As regard cultivars, PI280064 showed comparatively more variability for plant height, seed yield per plant and 25-seed weight, while variability was parallel in both the cultivars for other traits. In general, variability declined in M_3 compared to M_2 generation for most of the treatments, though the magnitude varied with the cultivar.

Phenotypic coefficient of variation (PCV) was invariably higher than genotypic coefficient of variation (GCV). Estimates of PCV, GCV and heritability were made group-wise using mutagen treatment means and

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mutagen treatmentwise using group means for the six traits in both the cultivars and generations. PCV and GCV varied with the generation, cultivar and trait and behaved parallel in group—and treatmentwise classifications. On an average, GCV was high in M_2 for plant height, number of pods per plant and seed yield per plant, while it was relatively high in M_3 for length of pod, number of seeds per pod and 25-seed weight in T163. PI280064 recorded relatively high GCV for most of the traits as compared to T163; it had high GCV in M_3 than M_2. PCV also showed a trend similar to GCV for all the six traits in both the generations and cultivars.

High heritability (h^2) was recorded in all the treatments as compared to control. h^2 estimates was high in M_2 generation for plant height, number of pods per plant and seed yield per plant in both the cultivars, while it was relatively high in M_3 for length of pod and number of seeds per pod. Group-wise h^2 was high for 25-seed weight, irrespective of the cultivars and generations.

On an average, recovery effects, as judged from the deviation of treatment means towards control from M_2 to M_3 with respective controls, were observed for all the traits in both the cultivars except 25-seed weight. It was remarkable to note decrease in CV with the corresponding increase in mean for seed yield per plant in M_3 while number of pods per plant, length of pod and number of seeds per pod recorded more variability as well as shift in means towards positive side. A decline in the magnitude of variability (PCV, GCV) from M_2 to M_3 was also noted, though varied to some an extent with the cultivar and trait.

Mutagen specificity was indicated by some of the traits. dES produced relatively more variability (PCV and GCV) and heritability for plant height, length of pod, number of seeds per pod and 25-seed weight, while both gamma-ray and dES were equally effective for number of pods per plant and seed yield per plant.

Genotype specificity, as judged from induced variability (CV), was noted; PI280064, which was found to be resistant as compared to T163 on the basis of biological parameters, also showed high variability (as judged from PCV and GCV) and heritability (h^2) for plant height, length of pod and seed yield per plant, while both the cultivars behaved similarly for other traits.

Efficiencies of treatments in terms of induced chromosomal interchange, chlorophyll mutations and quantitative variability were calculated; for estimates of efficiencies of micro-mutations for different traits, individual having different trait value, higher than the highest value of

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their respective control, were considered. Treatment efficiency varied with the cultivar and type of desirable mutation. Treatment with 10 and 15 Kr gamma-ray were found to be highly efficient for chlorophyll mutations and chromosomal interchange, respectively in both the cultivars. For micromutations, in general, 10 Kr gamma-ray was most efficient; treatment with 10 Kr gamma-ray was also at par with 0.5 dES at G_1 stage (for number of pods per plant) and 1.0% dES at S stage (for seed yield per plant) in the cultivar PI280064.

As regard groups, on an average, G_4 and G_5 recorded minimum shift in means; G_4 had high polygenic variability, while number of selected individuals with high seed yield were noted to fall in group G_5 and G_6 (4.35-4.58%) as compared to G_4 (2.17%).

On the whole, it might be concluded that treatment with 10 Kr gamma-ray may be used for getting high polygenic variability of desirable types, interchanges as well as chlorophyll mutations; treatment with 0.5% dES at G_1 stage may also be exploited for micro-mutations.

GENETICS OF SEMIDWARFISM AND YIELD TRAITS IN BREAD WHEAT (*TRITICUM AESTIVUM L.*)

Sup. *Dr. V. P Singh*

Poonam Singh

The present study was carried out to characterise the genetics of semidwarfism and yield traits in bread wheat (*Triticum aestivum* L.) through line x tester analysis, and the nature and magnitude of genetic variences, gene effects and combining ability (variances and effects) were observed. Heterosis, inbreeding depression, character associations and contribution of different traits directly or indirectly on plant height and grain yield were studied.

The nature of gene/genes in lines were detected by frequency distribution of height in segregating and backcross (F_1 crossed to its respective tester) generations. Identified lines for different dwarfing genes were tested for their responsiveness to exogenous gibberellic acid (GA_3) application.

Seventeen diverse wheat cultivars were chosen for the investigation, of which 13 cultivars of different heights were used as lines. The cultivars used as lines were : HD 2160, HUW 12, HD 2233, K 68, Sonalika, Janak, W 14-15, HUW SStd Anl 2, HUW Df 3, HUW Df Hp 1, C 2+2+13, W 12-1 and W10-6. Out of these cultivars as listed above, the first 6 were normal cultivars of bread wheat and remaining 7 strains were the mutants of K 68. The 4 testers of different dwarfing sources were Tom

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Thumb (*Rht*$_3$), Olsen (*Rht*$_{1+2}$), Kalyan Sona (*Rht*$_1$) and Sarbati Sonora (*Rht*$_2$), The 13 lines and 4 testers were crossed in line x tester design to produce 52 F_1s, 52 B_1s and 52 F_2s crosses. The final experiment was conducted during *rabi* 1981-82 in a Randomised Block Design with 3 replications.

Data were taken on randomly selected plants, 10 for parents and F_1s, 20 for B_1s and 50 for F_2s in each replication for 10 characters, namely, plant height, days to 50 per cent heading, peduncle length, number of ear bearing tillers per plant, number of grains per spike, length of Ist internode, length of IInd internode, total number of internodes, 100-grain weight and grain yield per plant.

The analysis of variance was carried out according to Panse and Sukhatme (1967). The line x tester analysis was performed according to Kempthorne (1957) and combining ability effects were estimated according to Singh and Chaudhary (1979). Average degree of dominance and heritability in narrow sense were calculated following the formulae of Kempthorne and Curnow (1961). Correlation coefficients were worked out according to the formula given by Panse and Sukhatme (1967) and path-coefficients were calculated according to Dewey and Lu (1959). Frequency distributions of plant height were graphically represented by individual plant data on height using 150 plants for F_2s and 50 plants for B_1s. The potence ratio in F_1 was calculated following the formula of Peter and Frey (1966).

Responsiveness to GA_3 application was observed by measuring the height of 15 days old seedlings in parental and F_1 populations at 0, 1 and 10 ppm concentrations of GA_3. Mean height in different concentrations of GA_3 was used for analysis of variance which was carried out according to Panse and Sukhatme (1967) and significant differences between means were tested by Duncan's multiple range test (Steel and Torrie, 1960).

Line x tester analysis was carried out into two groups. First group (group I) comprised 3 sets (i) 13 lines x 4 testers (set 1), (ii) 6 normal lines x 4 testers set (2), and (iii) 7 mutant lines $\times$ 4 testers (set 3); second group (group II) consisted of 4 sets of 13 lines x 3 testers. The 4 sets (i.e., sets 4, 5, 6 and 7) of 13 lines x 3 testers were obtained by eliminating one tester at a time from a set of 4 testers, for example, elimination of Tom Thumb (*Rht*$_3$), Olsen (*Rht*$_{1+2}$), Kalyan Sona (*Rht*$_1$) and Sarbati Sonora (*Rht*$_2$) was designated as set 4, set 5, set 6 and set 7, respectively.

It was envisaged from different sets that mutant lines contributed more towards non-additive genetic variance than normal lines or normal+

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mutant lines. The L x T analysis with 6 normal lines showed higher proportion of additive genetic variance in the inheritance of different traits in most of the cases except number of ear bearing tillers per plant. The magnitude of additive and non-additive genetic variances changed in the different sets of group I but the nature of the genetic variance remained unaltered. Preponderance of additive genetic variance was revealed by all the characters except number of ear bearing tillers in group I. The sets 2 and 3 revealed relatively higher proportion of non-additive genetic variances.

The L x T analysis with 13 lines x 3 testers in group II indicated similar inheritance pattern as was revealed by 13 lines x 4 testers analysis for most of the traits. However, genetic make-up of the testers had major influence on the inheritance of different traits rather than number of testers involved (3 or 4), e g., number of ear bearing tillers and 100-grain weight.

The average degree of dominance showed partial dominance for plant height, days to 50 per cent heading, peduncle length number of grains per spike, length of Ist internode, length of IInd internode, total number of internodes, and over dominance was observed for number of ear bearing tillers in all the sets. A change in the estimate of average degree of dominance was observed for 100-grain weight and grain yield per plant over different sets of line x tester analysis in the present study. 100-grain weight showed over dominance in all the sets except in set 2 while partial dominance was observed for grain yield per plant in set 2. The grain yield per plant exhibited over dominance in most of the sets.

Set 2 (6 normal lines x 4 testers) showed higher estimates of narrow sense heritability than the other sets of group I (i.e., sets 1 and 3), except for number of ear bearing tillers and total number of internodes. Narrow sense heritability was highest for plant height and moderate to high for days to 50 per cent heading, peduncle length, length of Ist internode, length of IInd internode and grain yield per plant in different sets of group I and II. Moderate to low estimates of narrow sense heritability were exhibited by number of ear bearing tillers (in all sets), number of grains per spike (set 3), total number of internodes and grain yield per plant (set 5).

In general, combining ability effects of the parents showed a good agreement with their *per se* performance. Best parents in F_1 also performed equally good in F_2. Parents, namely, Olsen, Tom Thumb, HUW Df 3, C 2+2+13, HUW Df Hp 1 and HD 2160 showed good general combining ability effects for height and its components. Sonalika, Kalyan Sona, W 14-15, W 10-6 and K 68 showed desirable combining ability

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effects for grain yield and its components. Parent HUW SStd Anl 2 showed desirable combining effects for number of ear bearing tillers and 100-grain weight but not for grain yield per plant. Parents HUW 12 and HD 2233 showed good general combining ability effects for dwarfness as well as for higher yield. These two were "tall dwarfs" among dwarfs with high potentials of yield. The parents which were good general combiner for yield also showed desirable general combining ability effects for one more yield components. Parent Sarabati Sonora was the best general combiner for days to 50 per cent heading only.

Usually the estimates of specific combining ability effects were higher in the F_1s than F_2s, except for days to 50 per cent heading, total number of internodes and grain yield per plant. There was disagreement between the *per se* performance of crosses and their sca effects. The crosses which showed significant sca effects in general included one good and the other poor general combiners. Desirable sca effects for dwarfness in most of the crosses were revealed when the combinations included one dwarf and other semidwarf or tall parents. The crosses, namely, C 2+2+13 × Tom Thumb in F_1 and K 68 × Olsen in F_2 showed good specific combining ability effects for grain yield per plant. Cross HUW SStd Anl 2 × Tom Thumb showed desirable specific combining ability effects for yield as well as for dwarfness also. The crosses which showed good specific combining ability for yield also exhibited desirable specific combining ability effects for atleast one of the yield components. i.e., number of grains per spike, number of ear bearing tillers and 100-grain weight.

Heterosis (over superior parent and economic check) and inbreeding depression were estimated for all the ten characters. Cross HD 2233 × Sarbati Sonora showed desirable heterosis (over superior parent and economic check) for dwarfness and also a good heterotic cross for grain yield per plant. W 10-6 × Kalyan Sona was the best heterotic cross (over superior parent) for grain yield per plant and also showed heterosis (over economic check) for number of grains per spike. HUW SStd Anl 2 × Tom Thumb was good heterotic cross (over superior parent and economic check) for grain yield per plant and also showed heterosis for length of Ist internode and length of IInd internode. HUW Df 3 × Tom Thumb was the best heterotic cross over both superior parent and economic check for smaller peduncle length with small inbreeding depression. Janak × Olsen and C 2+2+13 × Tom Thumb were the good heterotic crosses over both superior parent and economic check for number of grains per spike and their inbreeding depression were 11.81 per cent and 28.51 per cent, respectively.

The inbreeding depression for yield was also high ranging from—7.55 to 32.50 per cent. Most of the crosses showing higher heterosis were coupled with high inbreeding depressions.

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The correlation coefficients and path-coefficients were estimated for ten characters in 17 parents, 52 F_1s, 52 F_2s and 52 B_1s. The plant height exhibited positive and significant association with height and yield components, namely, peduncle length, length of Ist internode, length of IInd internode, total number of internodes, 100-grain weight and grain yield per plant. The height components, namely, peduncle length, length, of Ist internode and length of IInd internode showed association among themselves. The genotypic corre'ation coefficients were in parallelism with the phenotypic correlation coefficients, the magnitude of the former being slightly higher. Genotypic path-coefficients revealed that the direct effects of height components were substantially towards the correlation coefficients but the indirect effects of height components, such as, peduncle length, length of Ist internode, length of IInd internode and total number of inter nodes were also important. A significant positive association between yield and 100-grain weight was observed in all the 4 kinds of populations. The direct effects of 100-grain weight on yield was also high. Peduncle length showed negative direct effect on yield while its correlation was positive with yield. The grain yield showed a consistent picture of association with height and height components over the four populations. This indicates the importance of tall among dwarfs, i.e., "tall dwarf" selection for higher yield if the association of plant height with yield is viewed as an index of selection for high yielding types.

The direct path-coefficients in most of the cases were not in agreement with the simple genotypic correlation coefficients in different populations.

The frequency distribution graphs and variances of F_2 and B_1 populations for plant height revealed that the dwarfing genes *Rht*$_3$ and *Rht*$_2$ present in Tom Thumb and Sarbati Sonora, respectively are partially dominant over tall genes of K 68. On the other hand, the dwarfing gene *Rht*$_{1+2}$ present in tester Olsen showed partial recessiveness against the gene for tallness present in K 68. The tester Kalyan Sona possessing *Rht*$_1$ gene as dwarfing source exhibited additive type of gene action for plant height.

Out of 13 lines in the present study, 4 lines, namely, HUW 12, Sonalika, Janak and HUW Df Hp 1 showed unimodal peaks, lowest variances and ranges in F_2 and B_1 generations in the crosses of Sarbati Sonora containing *Rht*$_2$ as compared to other three testers. Potence ratio as estimated in the F_1 generation indicate that the F_1 means of the crosses of above 4 lines with Sarbati Sonora were close to mid-parental value except in Sonalika × Sarbati Sonora cross. Further, these varieties/strains were non-sensitive to exogenous GA_3 application in parental and F_1 populations. On the basis of aforesaid observations, lines HUW 12, Sonalika, Janak and

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HUW Df 1 were identified to possess Rht_2 gene for dwarfness. Similarly, variety HD 2160 was identified for Rht_{1+2} and HD 2233 for Rht_1 gene.

Most of the mutant lines (mutant derivatives of K 68) in the present study showed inconsistent behaviour in F_2 and B_1 generations with respect to range and variances, and unimodal peaks were not observed in the frequency distribution graphs for plant height of these lines crossed with different testers. Therefore, these lines could not be identified for the genes of height against the present set of 4 testers. One of the mutant lines, i.e., C 2+2+ 13 in the present study was exceptionally dwarf which showed a positive response to GA_3 application. Further, all the parameters used in identifying the gene/genes for height in the present study proved to be insufficient to identify the dwarfing source present in the mutant C 2+2+13.

Recommendations Based on Observations in the Present Study

The following recommendations are put forward :

1. Genotype/genetic make-up of the testers should be of broad genetic base in line × tester analysis.

2. Simultaneous importance of both additive and non-additive genetic variances as revealed in the present study for different traits in wheat indicated the need of suitable mating design which can incorporate both additive and non-additive gene effects. In this respect, intermating of segregants in early segregating generation has been emphasised by earlier workers which seems to be impractical seeing the self-pollinated nature of wheat. However, intermating in early segregating generation would be enhancing recombination in order to obtaind superior recombinant types and to accumulate favourable genes into an ultimate homozygous pure lines.

3. Correlation study should be supplemented with path-coefficient analysis for identifying direct and indirect influences of causal variables on the ultimate one.

4. Positive association between height and yield the indicated importance of talls among dwarfs, i.e., the "tall dwarfs" types would be most suitable for higher yield potentials.

5. *Per se* performance of the parents for different traits may be a suitable criterion for selecting parents with desirable gca effects.

6. Frequency distribution in F_2 supplemented by frequency distribution in backcross would be helpful in identifying the parents for dwarfing genes.

7. Exceptional dwarfness may not be necessarily related with major dwarfing genes, unless they are tested for their responsiveness to GA_3.

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HORTICULTURE

EFFECT OF NITROGEN AND GIBBERELLIC ACID ON VEGETATIVE GROWTH AND PHYSICO-CHEMICAL COMPOSITION OF CABBAGE *(BRASSICA OLERACEA L. VAR. CAPITATA)*

Sheo Achal Sup : *Dr. C. B. S. Rajput*

Field experiments involving four levels of nitrogen i.e. 0, 40, 80 and 120 kg/ha and gibberellic acid 0, 25, 50 and 75 ppm were carried out on cabbage cultivar Golden Acre at the Horticultural Farm, Institute of Agricultural Sciences, Banaras Hindu University, Varanasi, U. P., India during the year 1977-79. A number of growth observations, viz., height, fresh and dry weight of plant, number, fresh and dry weight of leaves, length and diameter of stem were recorded time to time during the period of research. Quality characters, viz. total sugar, ascorbic acid, nitrogen, phosphorus and potassium in open leaves and cabbage head were estimated. Growth characters were recorded at 25 days interval from transplanting generally at four stages of growth. Yield and yield attributing characters had been recorded at harvest.

All the growth parameters as referred earlier were greatly influenced by different levels of nitrogen and gibberellic acid. Maximum records for these characters were noted with the applications of $N_3 \times G_3$ combinations, followed by N_3 and G_3 treatments separately and were significantly superior than control as well as among themselves regarding a few of them. Yield and yield attributing characters had been found greatly influenced with the increasing concentrations of both nitrogen and gibberellic acid in both years. Maximum length, diameter, weight and yield of head were recorded under interactions of nitrogen and gibberellic acid during the period of research accompanied by a lesser variation due to climatic conditions. These were minimum under the absolute control in the year 1977-78 and 1978-79.

Most of the qualitative characters were influenced significantly in cabbage cv. Golden Acre in both years only excepting a few. The amount of total sugar percentage in head was maximum in N_2 and G_3 treatments of nitrogen and gibberellic acid in both years. However, all other treatments maintained their superiority over minimum results of control as regards the total sugar content of head was concerned. Ascorbic acid content was found highest with effect of interactions of N_3 and G_3 treatments of nitrogen and gibberellic acid in both open leaves and head of cabbage in

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both experimenting calander years of research work and lowest in control plant population. Rest treatments of nitrogenand gibberellic acid individually as well as in combinations were found intermediary in affecting the ascorbic acid percentage with a slight difference of action. The percentage of nitrogen, phosphorus and potassium of cabbage in open leaves and head were influenced significantly with the nitrogen and gibberellic acid treatments. The best percentage of all these elements were estimated from the sample of N_3 and G_3 treatments during conducting the experiment which were very closely followed by N_3 and G_3 treatments separately. The lowest value of N, P, K was recorded from the samples of control plants. All other treatments of nitrogen and gibberellic acid had generally shown their superiority over control. Moreover, there was a very clear cut picture of treatment variation in the series of effectiveness.

A very tangible effect of interactions of nitrogen and gibberellic acid applications was persistently observed regarding different vegetative growth, qualitative and yield characters constantly in both years. Use of nitrogen and gibberellic acid was very economical in cabbage production.

EFFECT OF GIBBERELLIC ACID, BORON AND CYCOCEL ON GROWTH, YIELD AND QUALITY OF TOMATO (*LYCOPERSICON ESCULENTUM MILL.*)

Basanta Kumar Bhoi Sup. *Dr. A. N. Maurya*

The stream of biological advancement which has flowed from the growth of tremendous scientific knowledge has almost revolutionised the very concept of life. This has led to the unfolding of many secrets of Nature which may easily be considered as landmarks in the history of Natural Science.

Hormonal research in India, which had long been in the background received a marked incentive in the recent past. As a result of such investigations, several fruitful observations have now been made, but the field of enquiry remains ruthless new and holds much for the future. This is particularly true because of the variety of climatic conditions that prevail and the many different plant species which grow in different parts in the country.

Micronutrient like boron played a vital role for healthy production of tomato. It not only affects the formation and accumulation of different

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fractions of carbohydrates but also its utilization in the normal physiological and metabolic processes in the plant.

Keeping in view of the importance of hormones and micronutrient, an attempt has been made to assess the effect of gibberellic acid, boron and cycocel on growth, yield and quality of tomato during the year 1981-82 and 1982-83. GA_3 and cycocel at required concentrations were sprayed over the whole plants of respective treatments, with a compressed hand sprayer. Teepol at 1 per cent was added to the aqueous solution as sticker. Only one spraying of GA_3 and cycocel were given at 20 and 30 days after transplanting respectively. Boron was applied at 25 days after transplanting as a single spray. The adjoining plants were saved by screening them with alkathene sheets. The control plants were sprayed with water only.

Observations on different growth characters were recorded from five randomly selected plants in each treatment. Observations on vegetative growth such as plant height, stem girth, number of branches and number of leaves per plant were recorded at 25, 50, 75 and 100 days after transplanting. And observations on flower number and fruit set were taken at 50, 75 and 100 days after transplanting. And observations on flower number and fruit set were taken at 50, 75 and 100 days after transplanting.

A factorial experiment, to study the effects of 27 treatment combinations comprising of 3 levels each of gibberellic acid (0, 25 and 50 ppm), boron (0, 1 and 2 ppm) and cycocel (0, 750 and 1500 ppm) on growth, yield and quality of tomato (*Lycopersicon esculentum* Mill.), was conducted at the Vegetable Experimental Farm of the Institute of Agricultural Sciences, Banaras Hindu University, Varanasi, during 1981-83, in winter seasons. The experiment was laid out in a randomise block design with three replications.

Plant growth, expressed in terms of height, girth of main stem, number of branches and leaves per plant and other characters like fresh and dry weights of shoot and root were best at high gibberellic acid concentrations. Number of flowers and fruit set, mean fruit weight, yield per plant, yield per hectare, number of ripe fruits harvested per plant attained maximum values at the high gibberellic acid application. Total soluble solids, ascorbic acid, reducing and non-reducing sugar content of fruits increased at high gibberellic acid concentration whereas number of seeds and fruit acidity declined to minimum at the same level.

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Similarly, boron at high level slightly reduced the height of the plant, girth of the main stem but increased the number of branches at the same level. It increased the number of leaves, number of flowers and fruit set per plant, yield per plant, yield per hectare, mean fruit weight at low concentration. The number of ripe fruits and titratable acidity were maximum at high level. Fruit T. S. S., ascorbic acid, reducing and non-reducing sugar contents were maximum at low level of boron application.

Cycocel was very effective in retarding the plant height. Decrease in main stem girth and number of leaves was also observed in the treated plants. But cycocel at low concentration improved branch number per plant. Fresh and dry weights of shoot and root were maximum at high concentration. Yield per plant and hectare, number of ripe fruits harvested per plant attained maximum values at the high cycocel concentration. The number of flowers and fruit set per plant were influenced by cycocel application. Mean weight of fruits declined in the cycocel treated plants. T. S. S. and sugar contents of fruits were found to increase at low concentration. However, the number of seeds, acidity and ascorbic acid contents gradually declined in the fruits of treated plants.

Plant growth expressed in terms of height was best in $G_1B_0C_1$ combination whereas the girth of the main stem and number of branches were maximum in $G_2B_2C_1$ combination. Fresh and dry weights of shoot and root were influenced by $G_1B_2C_2$. Similarly, number of flowers per plant and number of fruit set per plant were maximum at $G_1B_1C_0$ and $G_2B_0C_1$ combinations respectively. Days to ripening of fruits and mean fruit weight were influenced by $G_1B_1C_1$ and $G_2B_1C_1$ respectively. Number of seeds per fruit and number of ripe fruits harvested per plant attained highest values under $G_2B_1C_1$ and $G_1B_2C_1$ combinations respectively. Yields per plant and per hectare were maximum in $G_2B_0C_1$. Total soluble solids and non-reducing sugar content of fruits scored maximum value at $G_2B_2C_1$ whereas ascorbic acid and reducing sugar content of fruits were high in $G_2B_1C_0$.

Growth characters like plant height, girth of the main stem, number of branches and number of leaves scored significant and positive correlation coefficients with the yield. Similarly, number of fruit set per plant and number of ripe fruits harvested per plant were significantly and positively correlated with yield also. Amongst all, the last character, number of ripe fruits harvested per plant scored highest correlation coefficients with yield.

It might be concluded that 50 ppm gibberellic acid, 1 ppm boron and 750 ppm cycocel were most beneficial for the vegetative growth, flowering, fruiting and fruit quality of tomato.

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EFFICACY OF PLANT GROWTH SUBSTANCES ON GROWTH, YIELD AND QUALITY IN CABBAGE (*BRASSICA OLERACEA VAR, CAPITATA L.*)

H. N. Tutoo Sup. *Dr. V. S. Chhonkar*

The present investigation was conducted with the Golden Acre variety of cabbage (*Brassica oleracea* var. *capitata* Linn.) during the rabi seasons of 1980-81 and 1981-82 at Vegetable Research Farm, Banaras Hindu University, Varanasi and repeated during the summer season of 1981, under the temperate conditions of Srinagar at S. M. Farm, Haran; to study the efficacy of PGS like GA, NAA, IBA and IAA, when applied as seed, seedling and spray methods.

Varanasi is situated in the centre of North Gangetic alluvial plains on the left side of the river Ganga at an altitude of 128.9 metres above mean sea level and falls under the belt of semi-tropical and sub-tropical zone. The soils in general are alluvial loam of moderate fertility. While Srinagar (Kashmir) is situated at an altitude of 1616 metres above mean sea level and falls under temperate zone. The soil of the experimental site is clay loam of moderate fertility and having the pH 8.0.

The experiments were laid down under two sets. The first set of the experiment was conducted twice under field conditions at Varanasi and repeated once under climatic conditions at Srinagar. The treatments consisted of NAA 1 ppm, IBA 5 ppm and GA 10 ppm as seedling dip for 24 hr and spraying of whole plant with GA 5 ppm after two and three weeks of transplanting. The other set of the experiment, which was conducted once at both the locations (Varanasi and Srinagar), consisted of seed treatment. The seeds were soaked for 24 hr in NAA 40 ppm, IAA 20 ppm and GA 30 ppm before sowing and spraying of whole plant with GA 5 ppm, two and three weeks after transplanting. The main conclusions drawn from the results are summarised below :

(1) GA 10 ppm and IBA 5 ppm were found superior to NAA 1 ppm in facilitating quickest recovery of the seedlings.

(2) The use of PGS as seed treatment, stimulated the germination of seeds in nursery beds as well as in petri dishes. Early and maximum germination percentage was observed in the seeds treated with GA 30 ppm under both the locations, followed by IAA 20 ppm.

(3) Maximum leaf number was observed in the plants, wherein the seedlings were dipped in GA 10 ppm or IBA 5 ppm in early

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stage; whereas in rest of the stages of plant growth, GA 10 ppm seedling dip and given two sprays of GA 5 ppm (T_9), followed by T_7 (IBA 5 ppm dip + 2 sprays of GA 5 ppm) produced maximum leaf during both the years of plant growth. Under temperate conditions at Srinagar, maximum number of leaves was observed by T_7 followed by T_9. Rest of the PGS also showed significant increase when compared with control.

Plants raised from the seeds soaked in GA 30 ppm and given two sprays of GA 5 ppm after transplanting (T_9) also gave maximum number of leaves, followed by the plants given NAA 40 ppm seed dip + two sprays of GA 5 ppm after transplanting (T5). Rest of the treatments were also found superior to control. This trend of increase due to the PGS was observed at both the locations, with an overall increase under Varanasi conditions.

(4) The spread of the plants across the row exhibited marked variation at all the stages of growth. T_9 (GA 10 ppm seedling dip + 2 sprays of GA 5 ppm) showed significant increase in the spread of the plant than rest of the treatments, similar results were also observed in 2nd year. While at Srinagar maximum spread of the plant was shown by IBA 5 ppm treated transplants and given two sprays of GA 5 ppm after transplanting. Rest of the treatments were also found superior to control.

The plants under all the treatments of seed soaking with GA sprays after transplanting, showed larger spread than the control. T_9 (GA 30 ppm seed soaking + 2 sprays of GA 5 ppm) showed the maximum spread of the plant at both the location followed by T_5 (NAA 40 ppm + 2 sprays of GA 5 ppm).

(5) Height of the plant became more apparent after GA sprays and was found maximum in T_9 followed by T_7 under Varanasi conditions, during both the years of crop growth. However, under temperate conditions of growth, maximum height of the plant was recorded in T_7 followed by T_9. Rest of the treatments were also found superior to control.

Under seed treatment, maximum height of the plant was observed in T_9 followed by T_5, wherein the seeds were pre-soaked in GA 30 ppm or NAA 40 ppm and given two sprays of GA 5 ppm respectively. This trend of increase in height was recorded at both the locations.

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(6) All the PGS induced steady increase in the diameter of plants in initial stages. At harvest the maximum diameter of the plant was observed in T_9 followed by T_7 during both the years. At Srinagar maximum plant diameter at harvest was recorded in T_7 followed by T_9.

Under seed treatment too, there was no marked difference during the initial stages of plant growth in plant diameter due to PGS. However at the later stages of growth, the variation became apparent and the diameter of the plant was maximum in T_9 followed by T_5 at both the locations.

(7) The rate of development as well as the diameter of heads showed significant variations due to different treatments. All the PGS maintained steady increase in the diameter of heads over the control throughout the period of development. Maximum development of head size in both the year at Varanasi was observed in T_9 followed by T_7 and T_5. At Srinagar, significant differences were also observed since the initiation of head development and the highest diameter at harvest was observed in T_7 followed by T_9 and T_5.

Under temperate conditions at Srinagar, maximum diameter of the cabbage head was observed in T_9, wherein the seeds were pre-soaked in GA 30 ppm after transplanting. Seeds pre-soaked in NAA 40 ppm and IAA 20 ppm in combination with one or two sprays of GA 5 ppm were also superior to control. Similar results were also observed at Varanasi, with an overall increase in the head diameter in all the treatments than observed at Srinagar.

(8) The speedy and vigorous vegetative growth induced by PGS was markedly reflected in early head formation and uniformity. Seedlings treated with GA 10 ppm before transplanting and given two sprays of GA 5 ppm was found most effective in inducing early and uniform heads in cabbage plants in both the years. While as under temperate conditions of growth, seedlings treated with IBA 5 ppm and given two sprays of GA 5 ppm induced earliness and unformity. Rest of the treatments were also found useful to some extend in this respect, when compared with the control.

Under seed treatment, early initiation and uniformity of heads was seen in T_9 (GA 30 ppm pre-soaking dip + two sprays of GA 5 ppm) closely followed by T_5 or T_7. Rest of the treat-

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ments were also found superior to control. Almost similar trend was observed under Varanasi conditions also and the initiation and completion of head formation was found earlier than observed at Srinagar.

(9) Maturity of the heads was also affected with the PGS treatments. The results obtained at Varanasi in this respect are indicative of the fact that GA applied as seedling and spray methods proved beneficial in inducing earliness in picking maturity of head and the duration of picking maturity varied from 8 days in T_9 to 16 days in T_{12}. While as IBA as seedling treatment + 2 sprays of GA proved better under temperate conditions at Srinagar.

Under seed treatment, early and quick maturity of the head was observed in T_9 followed by T_5 or T_7. Rest of the treatments wherein the seeds were pre-soaked in NAA or IAA solution alone or incombination with one or two sprays of GA were also observed superior to control. At Varanasi similar trend with further earliness in the maturity of the heads under all the treatments was observed.

(10) The variation in root growth as induced by the PGS in different treatments showed very interesting results. Under all the locations, IBA 5 ppm treated plants, irrespective of GA sprays, effectively increased number, length and diameter of the lateral roots, followed by NAA 1 ppm treated plants. However GA 10 ppm treated plants were found superior to control.

Plants wherein the seeds were pre-soaked in NAA 40 ppm showed maximum number, length and diameter of lateral roots, recorded at two different stages under both the locations, followed by IAA 20 ppm. GA, however showed superiority over control.

(11) Studies on the yield of cabbage heads showed significant differences due to treatment effects and the maximum yield was observed in GA treatments (seedling treatment+two sprays). The extra yield of 204.44 q/ha was recorded in the said treatment than control. At Srinagar, plants treated with IBA 5 ppm before transplanting and given two sprays of AG 5 ppm produced highest yield, followed by GA treatments.

Under seed treatment, GA again maintained the supremacy as far as yield is concerned. Under both the locations maximum yield was obtained from the plants, wherein the seeds were pre-

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soaked in GA 30 ppm and given two sprays of GA 5 ppm after two and three weeks of transplanting. An extra yield of 175.55 and 239.63 q/ha was recorded in the said treatments than the control at Srinagar and at Varanasi respectively. Followed by T_5 (NAA 40 ppm dip+2 sprays of GA 5 ppm).

(12) No doubt PGS especially GA treatments helped to increase the size, volume or equator length of the head, but as far as compactness is concerned, control plants having the head size comparatively smaller showed much firmness than the p'ants treated with growth substances and was true at all the locations,

Similar trend regarding the compactness of head was observed under seed treatment trial also.

(13) Plants wherein the seedlings were treated with GA 10 ppm and given two spray of GA 5 ppm after two and three weeks of transplanting (T_9), increased the number of inner leaves to its maximum, followed by T_7 in both the years. While as at Srinagar maximum number was recorded in T_7 closely followed by T_9. IBA 5 ppm and NAA 1 ppm treated seedlings also showed significant increase in leaf number over control.

Plants wherein the seeds were given pre-soaking treatment with PGS, showed maximum number of inner leaves in T_9 followed by T_5 at both the places, with overall increase in all the treatments grown under Varanasi conditions.

(14) PGS significantly increased the size of the second outer leaf. Largest size of the leaf was recorded in GA treatment (T_9), followed by T_7, While as at Srinagar the results obtained showed maximum size in T_7. followed by T_9.

Under seed treatment and at both the locations, T_9 showed the maximum size of the second outer leaf. Rest of the treatments also showed significant differences when compared with control.

(15) The yield of outer leaves, which are very good for fodder was recorded maximum again in T_9 followed by T_7 in both the years and at Srinagar T_7 gaves the maximum yield of outer leaves followed by T_9. Rest of the treatments also showed superiority over control.

Plants given pre-seed treatment with GA 30 ppm and given two sprays of GA 5 ppm gave maximum yield of outer leaves at both the locations. The rest of the treatments showed signi-

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ficant differences over control. Thus, application of PGS not only increased the yield of head of the cabbage plant, but also increased the yield of outer leaves, which in turn add to the net profit from the crop.

Seedlings treated with GA or IBA and given two sprays of GA, contained less moisture, in the leaves forming the head. However, seedlings given water treatment or two sprays of water or control and the seedlings treated alone with NAA or IBA did not show any significant differences amongsts one another.

Treatments, wherein seed soaking was done either with GA or NAA and given two sprays of GA after transplanting, showed less percentage of moisture.

(17) Seedlings treated with GA and given two sprays of GA (T_9), proved effective to increase sugar and ascorbic acid content. However, seedlings treated either with GA or IBA and given two sprays of GA increased protein, P_2O_5, calcium percentages at all the locations.

Seeds pre-soaked in GA and given two sprays of GA after transplanting again showed increases in sugar, protein, P_2O_5, calcium and ascorbic acid content in the heads formed thereafter at both the locations.

(18) The percentage of magnesium content did not show significant variation due to the different treatments. However, acidity was markedly decreased in the heads of GA treated plants (T_9) over control at all the locations.

Again under seed treatment, percentage of magnesium did not show significant differences due to the different treatments. Acidity was markedly decreased in the heads treated with GA (T_9).

The above mentioned results of the investigation clearly show that GA applications either as seed or seedling treatment and given two sprays of GA, two and three weeks after transplanting, induced vigorous vegetative growth, higher yield of the heads having superior nutritive values, in comparison to control. NAA, IBA or IAA alone or in combination with one or two sprays of GA, were also effective in increasing the yield of the heads.

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STUDIES ON THE EFFECTS OF GIBBERELLIC ACID AND MALEIC HYDRAZIDE ON GROWTH, FLOWERING, FRUITING AND FRUIT QUALITY OF MUSKMELON (*CUCUMIS MELO L.*)

Lalji Ram Sup. *Dr. B. P. Singh*

An investigation entitled "Studies on the Effects of Gibberellic acid and maleic hydrazide on growth, flowering, fruiting and fruit quality of muskmelon (*Cucumis melo* L.) was undertaken with the following objectives.

(1) To find out the effects of gibberellic acid and maleic hydrazide on growth characters of muskmelon.

(2) To investigate the effects of gibberellic acid and maleic hydrazide on flowering and fruiting of muskmelon.

(3) To find out the effect of gibberellic acid and maleic hydrazide on fruit quality of muskmelon.

(4) To find out the combined effect of gibberellic acid and MH on growth, flowering, fruiting and fruit quality of muskmelon.

The experiment involved three levels each of GA_2 (O, 15 and 30 ppm) and MH (O, 150 and 300 ppm) were taken to find out their growth, flowering, fruiting and fruit quality of muskmelon (*Cucumis melo* L.) cv. Haramadhu, individually and in combination at the Vegetable Research Farm, Institute of Agricultural Sciences, Banaras Hindu University, Varanasi, during the year 1980 and 1981. A randomized block design was adopted with three replications. A number of growth observations viz., length of main creeper, diameter of main creeper, number of sub-creeper, length of sub-creeper, number of leaves per plant, area of leaves per plant, node number of first female flower, commencement of female flower, number of male flowers, number of female flowers, sex ratio, yield and yield attributes were recorded at periodical intervals. Quality characters as influenced by various treatments, viz., diameter of fruits, thickness of the pulp, diameter of seed cavity, moisture, T. S. S., sugar, ascorbic acid, protein in fruits and fresh and dry weight of leaf and plant were also observed.

Different treatments alone showed significant effects. As a whole treatments were found useful when applied in certain combinations. The highest concentration of GA_3 (30 ppm) and lowest concentration of MH (150 ppm) recorded beneficial.

All the concentrations of GA_3 stimulate the main axis and produced more number of sub-creeper in comparison to untreated plant. The MH

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treatment were found inhibitory effect on main axis and produced more number of lateral branches in comparison to all other treatments. Significant increase were also observed due to GA_3 and MH treatment in respect to other vegetative characters over control.

All the concentrations of MH applied caused the appearance of first female flower at lower nodes on the main axis, when compared with that of untreated plants. The lower concentration of GA_3 (15 ppm) also produced the pistillate flower at lower nodes than the control.

The MH treatments were found to be very effective in increasing the production of female flowers.

GA_3 at 30 ppm produced significantly more number of female as well as male flowers. This resulted high male/female ratio. The male/female sex ratio under MH was the lowest, as this plant regulator not only increased the number of female flower, but significantly suppressed the male flowers also.

The percentage of fruits harvested on the basis of female flowers produced were affected by plant regulators sprays. GA_3 (30 ppm) and MH (150 ppm) were also effective in increasing the fruit set.

The maturity period of the fruit was affected by plant regulators sprays, GA_3 (30 ppm) produced earlier fruits in comparison to MH and control.

All the concentrations of GA_3 and MH significantly increased the fruit number in comparison to control. GA_3 (30 ppm) and MH (150 ppm) were significantly superior to others.

The application of MH (150 ppm and 300 ppm) significantly decreased the fruit size, thickness of the pulp and diameter of seed cavity and GA_3 (15 ppm and 30 ppm) significantly increased the fruit size, thickness of the pulp and diameter of seed cavity in comparison to all other treatments.

The experiments have conclusively brought out that the yield of muskmelon can be increased by the modification of sex with exogenous application of plant growth regulators.

The application of GA_3 (30 ppm) and MH (150 ppm) emerged out the most effective in increasing the number of female flowers and ultimate yield.

With regard to quality, moisture, T. S. S., sugar, ascorbic acid and protein content, all were increased due to gibberellic and maleic hydrazide sprays. Fresh and dry weight of leaf and plant was also increased due to above treatments.

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Thus the experimental evidences warrant the following specific conclusion, which may in general be adopted for profitable cultivation of muskmelon.

To have better optimum growth, yield and quality of muskmelon of cultivar 'Haramadhu', the application of 30 ppm of GA_3 and 150 ppm of MH is very useful.

EFFECT OF PLANT REGULATORS ON GROWTH, FRUITING AND FRUIT QUALITY IN BER (*ZIZIPHUS MAURITIANA LAM.*)

Chhabi Nath Singh Sup. *Dr. C. B. S. Rajput*

The present investigations entitled Effect of plant regulators on growth, flowering, fruiting and fruit quality in ber", was coducted in the research orchard of the Department of Horticulture, Institute of Agricultural Sciences, B. H. U., Varanasi, India during 1979-81. The experimental variety Banarasi Karaka was treated with the foliar application of GA_3, planofix and 2, 4, 5-T each at 20, 40 and 60 ppm concentrations. Water spraying was done as a means of control for each replication. With due intervals spraying treatments were done twice in a year i.e. September and October. Observations were regularly recorded on various growth aspect, flowering, fruiting and physico-chemical composition of the fruit and leaf nutrient content.

Experimental technique was framed in the pattern of Randomised Block Design and the data obtained were statistically analysed. Improvement in the vegetative growth revealed in significance as per the record of the treatment done by GA_3, planofix and 2, 4, 5-T at various concentrations in term of length of terminal shoot, number of leaves and leaf, area. The rate was seen to be rapid in beginning as compare to later stages.

These foliar application proved to be significantly effective in improving the number of flowers and fruit set percentage per shoot. Control of the fruit drop and increase in the fruit retention capability showed marked improvement as result of these treatments.

As per the physical character of the ber fruit is concerned which excelled after the periodic sprays of the plant growth substances.

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Significant exhibition was the effect on fruit length and diameter with limitation in stone length, weight and diameter which met with reduction. On the other hand fruit weight, pulp weight and yield were considerably higher.

Of no doubt, as per the results the role played by plant growth substances had to after the chemical constituents of the fruit in a modified line. The results in the bright line of improvement was the total soluble solids; whereas, the reduction in acidity percentage had been the dark side. But increase in the percentage of sugar of both reducing and non-reducing were the marked effect of the treatments. Remarkable improvement was observed in the content of ascorbic acid and pectin. Comparatively G_3 and P_3 performed well.

Dry weight content of leaves gained a heightened level under the effect of these treatments. But the balanced effect could not be seen in case of nitrogen, phosphorus and potash content of the leaves which revealed a downfall.

Higher levels of nitrogen content were seen under the treatments of G_3, whereas minimum in case of control. Likely the phosphorus and potash content was found higher in G_3 and viceversa in control.

On analysing and accounting the overall performance of these varied treatments it is concluded that gibberellic acid can be ranked on the top.

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MYCOLOGY AND PLANT PATHOLOGY

STUDIES ON RHIZOSPHERE MYCOFLORA OF MUSTARD (*BRASSICA JUNCEA L. CZERN AND COSS*) IN RELATION TO *RHIZOCTONIA SOLANI* KÜHN

S. N. P. Chaurasia Sup. *Dr. R. Dayal*

Normal development of human body needs proper and balanced diet. In our daily balance diet, fats and oils have important place with other cereals and pulses. Among the oils used, mustard oil occupies an important place because of its special type of flavour. The mustard is cultivated as annual herb and generally called 'Sarson' in India.

Government of India is diverting their foreign exchange valued Rs. 600 crores to other country for the import of the rape and mustard oil which is next to that on petroleum products. The main reason of shortage and high price of edible oils in the country are due to stagnant level of productivity, rising internal demand of an increasing population, non-availability of new area for oil seed cultivation and disease problem. A number of organisms causing disease have been reported attacking the crop. A damping-off of mustard seedlings was observed during the year 1977-78, caused by *Rhizoctonia solani* Kühn *(Thanatephorus cucumaris)* (Frank.) Donk).

The intensity of disease occurrence was found between 5-14% during the study period. The pathogen reduces the number of healthy seedlings and ultimately loss in production. The control of soil-borne plant pathogens by the use of chemicals have proved uneconomical because, it provides temporary control. It also changes the ecological balance of soil ecosystem and brings a problem of pollution. Biological control may lead to a permanent solution in control of soil-borne plant pathogens. The present investigation was undertaken to study the ecology of *Rhizoctonia solani* causing damping-off of mustard seedlings which may provide a significant clue for control and management of the diseases.

Quantitative and qualitative analysis of rhizosphere mycoflora of three mustard *(Brassica juncea)* cultivars viz., PR-6, PR-10 and RW-175 were made in relation to plant age, variety and pathogen. The isolation of rhizosphere mycoflora was made at an interval of 15, 30, 45, 60, 75 and 90 days old plants. In all a total of 172 fungal species were isolated, out of which 9 belong to Phycomycetes, 8 to Ascomycetes, 145 to Deuteromycetes, from rhizosphere and non-rhizosphere. Similarly, from the rhizoplane, 48 species were isolated, out of which 2 belong to Ascomycetes and 46 to

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Deuteromycetes. The fungal population increased with increase in the age of plant in all the three cultivars upto 60 days followed by a decline. Different varieties exerted somewhat different rhizosphere effect at different ages both quantitatively and qualitatively. The damping-off pathogen *R. solani* was rarely isolated in the rhizosphere of healthy plants in all the three varieties. Fungi/g of dry soil of diseased plant was found much more than the rhizosphere of healthy plants. *R. solani* was found frequently from rhizosphere of diseased plants in all the three varieties. Rhizoplane fungal population was always less than rhizosphere population. Fungal activity and percentage colonization exhibited no difinite trends on root surface but different varieties exerted somewhat different rhizoplane effect. The pathogen *R. solani* was isolated from rhizoplane of all the three varieties at all stages of plant growth except 15 days old seedlings. The fungal activity and percentage colonization in rhizoplane of diseased seedling was much more than healthy plants. The rhizoplane of diseased plant was generally colonized by *Fusarium oxysporum*, *R. solani* and white sterile mycelial forms.

Impact of fungi on seed is considerable because, its presence directly influence the quality, health, nutritional value, germination and ultimately crop stand in field. Seed mycoflora of three varieties of *B. juncea* was investigated. Total 46 fungi were associated on seeds of the three cultivars. *Alternaria alternata*, *A. brassicae*, *Aspergillus terreus*, *Chaetonium globosum*, *Cladosporium herbarum*, *Curvularia lunata*, *C. pallescens*, *Drechslera australiensis*, *F. oxysporum*, *F. solani*, *Nigrospora sphaerica*, *Penicillium janthinellum* were found associated with all the varieties.

Ten species, *Alternaria brassicae*, *Alternaria* sp., *Aspergillus flavus*, *A. nidulans*, *A. niger*, *Cladosporium herbarum*, *Curvularia lunata*, *Fusarium oxysporum*, *F. solani*, *Penicillium citrinum* and *Phoma* sp. were isolated from internal seed coat of all the three varieties. A significant correlation was observed between external and rhizoplane mycoflora at the seedling stage. *R. solani*, causal agent of damping-off was found non seed borne in nature on mustard seeds in our studies.

Increased amount of microbial products and synthesis of growth factors in the root zone exert some effect on plant growth. Effect of culture filtrate of 16 fungi occurring in rhizosphere and rhizoplane, on the seed germination and radicle growth of *B. juncea* Var. PR-10 was made. Culture filtrates of all the test fungi significantly inhibited the germination of seed to different degrees. Culture filtrate of *Trichothecium rosceum* was found most effective in inhibiting the germination of seeds. Similarly, radicle growth was also significantly inhibited by culture filtrates of all the test

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fungi. Maximum inhibition in radicle growth was observed in case of *Acrophiliaphora fusispora* and change in pH of liquid medium was also observed.

Effect of 16 rhizosphere and rhizoplane fungi on root growth of seedling of *B. juncea* Var. PR-10 was studied on nutrient agar medium. All the test fungi significantly inhibited the root development. The roots of seedlings were found rotten in the case of *R. solani.*

The microbial interactions in soil involve diverse micro-organisms which influence the behaviour and survival of individual species. This results antagonism which have direct or indirect effect on individual or population against others. The effect of non-volatile and voltaile metabolites of some selected mycoflora was studied on growth behaviour of the test pathogen The inhibitory effect of non-volatile metabo'ites of the test fungi against *R. solani* was found. The non-volati'e metabolites of *Trichothecium roseum* and *Aspergillus niger* exhibited most pronounced inhibitory effect on the *R. solani* growth. The volatile metabolites of *T. roseum* and *Penicillium jenthenillum* showed maximum inhibitory effect on radial growth of the test pathogen while volatiles of *Acremonium terricola*, *Aspergillus flavus*, *A. niger* *Fusarium oxysporum*, *Neocosmospora vasinfecta* and *Stachybotrys atra* exhibited no significant inhibitory result on colony diameter of the pathogen. In hyphal interference and mycoparasitic studies of the test fungi with *R. solani*, only *A. niger*, *Gliocladium roseum*, *Trichoderma harzianum* and *T. roseum* were recorded as a mycoparasite. *A. niger* and *T. roseum* were recorded as a mycoparasite of *R. solani* for the first time.

In another studies, antagonistic interaction of two isolates of *Trichoderma herzianum* and one isolate of *Trichothecium roseum* was studied at different temperature. The non-volatile metabolites of *Trichoderma harzianum* I was found most effective in the inhibition of colony diameter of the test pathogen at 25±2°C whereas non-volatile metabolites of *T. roseum* were effective at all temperatures in inhibition of colony diameter of *R. solani.* Volatiles of *T. harzianum* I stimulate the colony growth at 20 ± 2°C. The best effect of volatiles on colony diameter of the pathogen was recorded at 25 ± 2°C. Higher temperature exhibited less effect.

Control of *R. solani* by the two mycoparasite *T. harzianum* and *T. roseum* was recorded. They reduced the disease intensity to 34 and 40% in first year and 4% in second year experiment.

Competitive saprophytic colonization of the host substrate by the test pathogen in relation to soil temperature, pH, moisture content, soil

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amendments with fungicides, fertilizers, oil cakes and precolonized root segments of the host was studies. The most suitable temperature for the best competitive saprophytic ability of the pathogen was found to be 25 ± 2°C. At higher temperature the substrate was vigourously colonized by *Aspergillus nidulans*, *Chaetomium* sp., *A. niger*, *Populospora* sp. and *Curvularia lunata* which suppressed the colonization of substrate by *R. solani*. High competitive saprophytic colonization of host substrate by *R. solani* was noted at pH 7.00 and 7.6. Moisture level between 20-30% favoured the saprophytic colonization of host substrate by *R. solani*

Saprophytic colonization of host substrate by *R. solani* decreased in soil amended with fungicides. Benlate and Demosan were found most effective fungicides at 0.5% concentration where C_{50} value was zero. Dithane Z-78 was found less effective. Demosan and Benlate were most effective at 0.25% concentration where C_{50} value was zero and 0.5, respectively. The oil cakes also inhibited the competitive saprophytic colonizing ability of *R. solani*. Neem oil cake was found most effective in reduction of the saprophytic activity at 4 and 2% amendment to soil while Mahuwa cake was least effective. Urea and NPK enhanced the saprophytic activity of *R. solani* at both the concentrations applied to the soil. The phosphatic and potassic fertilizers have no effect on the activity.

The saprophytic colonization of the root substrate units by *R. solani* was found to reduce when the segments had already been colonized by other fungi. *T. roseum* precolonized root segments have strong activity against *R. solani* while *Acremonium terricola* was less effective.

Propagules of soil-borne plant pathogens remain resting in soil either because of inherent dormancy or because of ecological factors of soil ecosystem. These factors mostly contribute to fungistasis. Fungistatic activity of experimental field soil was determined against *R. solani*. The soil exhibited insignificant fungistatic activity with the pathogen. The activity decreased rapidly from October to a minimum in January-March and then increased. Amendments of oilcakes and fungicides to the soil enhanced the fungistasis. Neem oil cake was found best for the elevation of fungistasis and fungal population whereas Demosan amended soil exhibited maximum fungistasis in both the months. The fungistatic activity of different soil samples against *R. solani* was assessed in relation to soil pH, percent organic matter, fungi/g of dry soil and percent moisture content. There was no definite correlation between volatile and non-volatile fungistasis and, therefore, their origins are different. High fungistatic activity was exhibited generally by the soil having high organic matter. The soil pH has insignificant impact on fungistasis.

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Decomposition of plant residue and other organic matter by soil microbes is an absolute pre-requisite comprehension of factor determining the longevity of saprophytic survival of root infecting fungi. During saprophytic colonization of dead tissues the fungus established a mycelial network throughout the tissues and thereby the fungus survives saprophytically by a slow but continuous exploitation of available nutrients. Cellulolytic activity of the pathogen was determined under a range of physical and nutrient condition, using a weight loss method. Significant interaction between enviornmental factors was encountered. Maximum cellulolytic activity of the pathogen was on filter paper wads (with nutrients) while other cellulose substrate exhibited lesser activity. Increase in nitrogen concentration/litre increases the cellulolysis. At higher concentration the cellulolysis was reduced insignificantly. Different nitrogen sources exerted somewhat different cellulolytic activity. Urea and ammonium nitrate were found best for the activity of the pathogen. The activity was maximum at 25 ± 2°C and pH 7.00. Alternate temperature of 15 and 25 ± 2°C was more effective on cellulolytic activity than other temperatures tested.

TAXONOMIC STUDIES ON SOME INOPERCULATE DISCOMYCETES

Shishir Kumar Gautam Sup. *Dr. D. C. Pant*

In this thesis a brief account of the morphology, distribution and variability of the discomycetes has been provided. Following the usual practice the major differences between the operculates and the inoperculates have been given as regards the general appearance, tissue structure, ascal tips and the characters of the ascospores in both the groups.

The economic importance of these fungi, especially the inoperculates, has been summarised. Their roles in the decomposition of forest litter and in the formation of lichen thalli is emphasised, while at the same time enumerating the more important parasitic species causing diseases of higher plants.

The published anamorphs of the inoperculates have been listed together with their apothecial genera (telomorphs).

A review of the works of early botanists as well as those of the current workers in the field of discomycetes has been presented. Emphasis has been laid on the work of mycologists who have studied Indian species.

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Most of the fungi reported in this work were collected from forests ln Uttar Pradesh and West Bengal (39 species) but one each of the remainder two species were obtained from Coorg Dist. Karnataka and Khurda Road, Orissa respectively.

These fungi were studied in fresh condition for their growth habit, colour, size and shape of the apothecia, whereas, freezing microtome sections were made from rehydrated material in the laboratory for microscopy.

A total of 41 species belonging to thirteen genera in five families were studied in this work and analytical keys have been provided for those taxa where their number was two or more. These are listed below :

Families	Genera	Number of species
Sclerotiniaceae	*Lambertella*	3
	Lanzia	8
	Poculum	2
	Moellerodiscus	1
Orbiliaceae	*Orbilia*	1
Dermateaceae	*Tapesia*	1
	Mollisia	1
Hyaloscyphaceae	*Psilachnum*	1
	Dasyscyphus	4
Leotiaceae	*Neobulgaria*	1
	Phaeohelotium	1
	Cyathicula	2
	Hymenoscyphus	15

These species have been critically examined for their identification, and have been compared with the specimens of the same species if available in Punjab University Herbarium (PAN) Chandigarh. In other cases the comparisons have been made with the published descriptions and illustrations of the type or authentic materials.

In this study 15 species new to science and one new variety were encountered. In addition 11 other species are being reported for the first time from India. These are as follows :

(A) **New species**

(i) *Lambertella crystallina*, (ii) *L. whetzelii*, (iii) *L. sukunaensis*, (iv) *Lanzia foliicola*, (v) *L. moniliformae*, (vi) *L. bucklandicola*, (vii) *Moellerodiscus aucubacolus*, (viii) *Tapesia pulviniformata*. (ix) *Psilachnum Macrofructus*, (x) *Neobulgaria angustispora*, (xi) *Phaeohelotium*

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fractosum, (xii) *Hymenoscyphus praecoxascens*, (xiii) *H. vermiformis*, (xiv) *H. parvifructus*, and (xv) *H. perpusillus*.

(B) **New variety**

Hymenoscyphus phyllophilus var. *rhizocola*

(C) **New records**

(i) *Lanzia rufocornea*, (ii) *L. luteovirescens*, (iii) *Orbilia leucostigma*, (iv) *Mollisia pastinacae*, (v) *Cyathicula helios*, (vi) *Hymenoscyphus vitigenus*, (vii) *H. flavo-fuscescens*, (viii) *H. imberbis*, (ix) *H. rhodoleucus*, (x) *H. dearnessii*, and (xi) *H. robustius*.

Some of the new taxa have already been published whereas the others are in the process and should appear in the coming months.

STUDIES ON ZOOSPORIC FUNGI

Km. Nandita Sarkar Sup. *Dr. R. Dayal*

The term aquatic Phycomycetes applies to the zoosporic coenocytic fungi which live in water or soil as saprophytes or parasites on various plants and animals or their parts, in water or in damp soil, and produce flagellate motile asexual reproductive structures known as zoospores.

In recent years aquatic fungi have received considerable attention. This may account for the increased interest in aquatic organisms. Pollution of streams, rivers and local shores is common, therefore, the role of microfungi, in this situation is important. Recent researches suggest that aquatic fungi may play a key role in the productivity of streams, estuaries and rivers. The role of these fungi in water are of many types e. g., they take part in the degradation of oil in the marine environment by the bio-degradation of hydro-carbon compounds. They also act as intermediaries of energy flow in streams by playing a key role in unlocking and distributing a major source of energy. They are also responsible for the pollution in sewage water system. Fungi contribute to the energy flow and productivity of aquatic ecosystems by their existence as a source of carbon as well as by their active metabolism on suitable substrates. They also act as biological indicator, and also take part in self-cleansing process.

Keeping their importance in mind, the ecological and taxonomical studies of these fungi have been undertaken.

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In the beginning an introduction of these fungi has been given which includes their definition, importance, role in aquatic ecosystem, occurrence and a description of zoospore structure, thallus, asexual and sexual reproduction, including both Uniflagellatae and Biflagellatae i.e., Chytridiomycetes, Hyphochytridiomycetes and Oomycetes.

A brief account of the work done so far, on the taxonomical and ecological aspects of these fungi has been given in historical resume.

The materials and methods used for the collection, isolation, detailed observation and preservation of these fungi have been given and also the method used to calculate temperature, specific gravity, pH, chloride content and dissolved oxygen. The detailed quantitative estimation methods have also been given.

Ecological studies include the observations on percentage occurrence and seasonal occurrence of 44 zoosporic fungi. The effect of different factors, viz., temperature, specific gravity, pH, chloride content and dissolved oxygen, on these fungi have been observed. Both qualitative and quantitative estimations have been made. The results have been given in 17 Tables and 22 Plates for graphical representation. Percentage occurrence studied, showed that among chytrids *Rhizophlyctis* spp, and *Rhizidium* spp. and among Saprolegniales, *Achlya* sp. and *Aphanomyces* sp. were most dominant.

Seasonal occurrence of these fungi was also studied. It showed that autumn and spring were the two best seasons in the year for the growth of chytrids whereas winter was best for Saprolegniales, and Peronosporales were found almost all the year round. Number of propagules were counted by quantitative estimation method. The results of these estimations showed that there was an increase and decrease in the number of propagules with the change in season. Autumn was best season for the growth of *Allomyces* sp. and the highest number of propagules were found during this period. Propagules of *Achlya* sp. and *Aphanomyces* sp. were found from rainy season to winter end, the highest number of propagules of *Achlya* sp. could be seen during winter and those of *Aphanomyces* sp. during autumn to early winter. Propagules of *Saprolegnia* sp. could be isolated during winter, as also those of *Dictyuchus* sp. propagules of *Pythium* sp. could be isolated throughout the year and they were specially abundant during winter.

Effect of several factors on the occurrence of these fungi has been studied.

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Temperature has a profound effect on the occurrence of zoosporic fungi. Chytrids preferred a moderate temperature range, whereas low temperature was suitable for the growth of biflagellates.

A very high specific gravity relates to polluted water and a very low relates to clear water. Chytrids preferred a moderate specific gravity levels whereas Saprolegniales preferred a low level. Peronosporales occurred at all the specific gravity levels except a very high one. The number of fungal propagules decreased with an increase in specific gravity.

pH is an important factor in determining the presence or absence of a particular species. The results show that zoosporic fungi preferred slightly alkaline pH. Quantitative estimations show that number of propagules increased with the increase in pH.

Different genera of Chytridiales and Blastocladiales, differed in their chloride requirement. Saprolegniales preferred low level, whereas Peronosporales could tolerate a wide range. Quantitative studies showed that there was a decrease in the number of fungal propagules with the increase in chloride content.

Dissolved oxygen is an important factor determining the presence, absence and/or formation of sex organs etc., of zoosporic fungi. Chytrids preferred a moderate level of dissolved oxygen. Blastocladiales required low oxygen level whereas Saprolegniales, always occurred during a period of high dissolved oxygen content. The number of propagules increased with the increase in this factor.

In the taxonomical portion the taxonomic criteria, used in the classification of these fungi have been discussed, followed by taxonomy of these fungi. The taxonomic description includes an illustrated detailed account of 23 species, belonging to 11 genera and distributed in 7 families. Among these, 13 are being reported for the first time from India, and a new variety has been created. These fungi were distributed in 6 orders-Chytridiales, Blastocladiales (Chytridiomycetes) and Hyphochytriales (Hyphochytriomycetes), Saprolegniales, Lageridiales and Peronosporales (Comycetes).

From Chytridiales, the detailed description of the following fungi were included :—

Rozella allomycis, Dictyomorpha dioica, D. dioica var. *pythiensis, Rhizidium varians* and its ten forms, *R. elongatum, Rhizophlyctis spinosa, R. chitinophila, R. petersenii, R. hyalina* and its one form, *R. willoughbyii* and its 3 forms, *Rhizophlyctis* sp. 3, *Karlingia marylandia, K. chitinophila, Karlingia* sp. and *Septochytrium marylandicum.*

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Among these, *Dictyomorpha dioica*, *Rhizophlyctis spinosa*, *R. chitinophila*, *Karlingia chitinophila* and *Septochytrium marylandicum* are new records from India.

Among Blastocladiales, the detailed description of *Catenophlyctis variabilis* has been given.

Saprolegniales which have been described in detail include *Saprolegnia ferax* and its one form, *S. eccentrica*, *S. hypogyna* and *Aphanomyces helicoides*. Among these, *Saprolegnia eccentrica*, *S. hypogyna* are new records from India.

From Lagenidiales, *Olpidiopsis luxurians* was described.

Peronosporales include the detailed description of *Pythium torulosum*, *P. apleroticum* and *P. aphanidermatum*. *P. torulosum* and *P. apleroticum* are new records from India.

STUDIES ON *SCLEROTINIA* WILT AND ROT OF GRAM (*CICER ARIETINUM* L.)

Ram Bahadur Singh Sup. *Dr. U. P. Singh*

Sclerotinia sclerotiorum (Lib.) de Bary, being a cosmopolitian plant pathogen, is one of the most economically important inoperculate discomycetes which causes significant losses to gram (*Cicer arietinum* L.) crop in cool and humid areas of Uttar Pradesh. The loss in general ranges from negligible to extensive. Although the pathogen, being soilborne, is known to occur on gram since long in India, its occurrence has been observed only recently in the vicinity of Varanasi occasionally in the epidemic form in recent years.

The annual recurrence of this disease in mild to highly destructive form prompted initiation of an intensive research programme to understand in detail its biology and various factors which interact to enhance or delinit its ability to produce disease, and its economic control measures under laboratory and field conditions.

Symptoms produced by *S. sclerotiorum* on gram plants were observed during the successive growth of the plants. Infection is usually more abundant after initiation of blossom stage. Early disease symptoms appear as soft, watery spots on stem branches and leaves. White mycelial growth soon develops around these spots under cool and moist condition followed

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by the production of resistant bodies called sclerotia. The branches and leaves later gradually die and exhibit a white punky appearance. The sclerotia over summer in the soil and produce mycelia or apothecia under favourable conditions in the next season thus completing the whole life cycle.

The pathogen was isolated from infected plant parts in artificial medium. Pathogenicity test was carried out using both mycelium and ascospores, and typical wilt and rot symptoms developed on gram plant after 4 to 7 days. Reisolations from these infected parts always yielded cultures typical of *S. sclerotiorum*. The pathogen was tentatively identified as *S. sclerotiorum* (Lib.) de Bary on the basis of morphological and cultural characters. Cultures of *S. sclerotiorum* were further processed for soluble proteins, aromatic esterase and tetrazolium oxidase by gel electrophoretic method, and compared with Wong's isolates of *S. sclerotiorum*, *S. minor* and *S. trifoliorum*. The results revealed that gram isolates are typical *S. sclerotiorum*. This reconfirmed the identity of *S. sclerotiorum* occurring on gram in India.

Almost 90% of the life cycle of *S. sclerotiorum* is spent in soil as sclerotia under certain conditions, depending upon various environmental factors and inherent nature of the fungus, sclerotia germinate and form either mycelium or apothecia to produce ascospores and both can cause infection. Although mycelium produced from sclerotia has been considered a possible means of infection of the host plants, the major source of inoculum is ascospores. Consequently it can be presumed that the factors affecting sclerotial germination, either myceliogenic or carpogenic, and growth of the pathogen may be determining disease incidence during the crop season. Therefore, effect of sclerotial exposures to different temperatures for varying periods of time on germination, growth, sclerotia formation and survival was observed. High temperature for longer periods affected these processes. Out of 6 synthetic and 3 natural media, SP_3 medium was best for quick germination of sclerotia, maximum number of sclerotia/plate, highest percentage of carpogenic germination and maximum number of apothecia/sclerotium. Rich nutrition may be the possible attribute for the best performance of SP_3 medium.

Apothecia were produced on sclerotia either burried in different types of soils, placed or floated on different substrata. Maximum germination, number of stipes and mature apothecia/sclerotium were noticed in sclerotia incubated in sterile distilled water.

The effect of different monochromatic lights, viz., blue (450 nm), green (545 nm), red (650 nm) and white light, individually and in combi-

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nation, on germination and apothecia formation in *S. sclerotiorum* was also observed. Blue light, in comparison to others, induced rapid germination and apothecia formation whereas red light was inhibitory. The inhibitory effect of red light was reversed following post-treatment of sclerotia with blue light for 8 hours.

The anatomical studies of apothecia formed under different lights revealed that although the large size of apothecia produced under white light exhibited increase in all types of cells/reproductive structures, nevertheless, the major increase was observed in the hymenial cells accounting for the increase in total size of the apothecia.

Similarly, effects of soil texture, soil mixture, depth of burrial and soil moisture was observed on carpogenic germination of the pathogen. Sclerotial germination occurred more profusely in light soils. Increase in clay content of the soil suppressed germination and apothecia formation. Sclerotia did not germinate at 5%, 50% and 50% soil (sandy loam) moisture levels whereas maximum germination was observed in soils having 30% moisture.

Sclerotia kept at surface of the soil germinated readily and produced mature apothecia in all the soil types. However, less stipes were produced in those kept at shallow depths. Deep burrial inhibited germination. During the production of apothecia from sclerotia, a number of anomalous types were formed when the incubation temperature was raised to more than 20°C with concurrent depletion in moisture content.

The earlier method of collecting ascospores from apothecia of *S. sclerotiorum* for their use in inoculation/cytology and other studies, was modified. Development of the pathogen on various stages of gram plants right from germinating seed to 3-week-old seedlings and also on detached parts of gram by mycelium and ascosporest of the pathogen was studied. Infection occurred readily in the blossom followed by at collar region of the host stem. Mechanical pressure seems to be of major importance in initiating penetration of host tissues. There was a positive correlation between plant age and infection of host by ascospores.

Differential responses of host and non-host substrata on germination of ascospores of *S. sclerotiorum* was observed. Maximum germination was noticed on flower petal of gram with minimum time for germ tube, initiation. Among the non-host substrata germination was completely inhibited on ginger (*Gingiber officinale* Roscae.) rhizome-peelings. However, the germination was delayed (after 12 hr) on rhizome peelings of turmeric (*Curcuma longa* L.).

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Studies on nuclear behaviour and anastomosis in vegetative hyphae of *S. sclerotiorum* were carried out. The vegetative hyphae were multinucleate. The morphology and nuclear number/cell varied with the age of hyphae. In hyphal tips the number of nuclei ranged from 2-4/cell while 50-59 in older hyphae. The nuclear migration from one hyphal cell to another following anastomosis was observed.

During a survey of gram crop, *S. sclerotiorum* was noticed to infect several weed plants, e, g., *Ageratum conyzoides* L., *Launea nudicanlis* Hkf. (Compositae), *Convolvulus arvensis* L. (Convolvulaceae), *Cyperus rotundus* L. (Cyperaceae), *Desmodium triflorum* DC., *Vicia sativa* L. (Leguminosae) and *Anagalis arvensis* L. (Primulaceae). All the plants exhibited stem and leaf rot symptoms. The pathogen was isolated on PDA from infected hosts separately and each isolate was found to be pathogenic to all the plants during cross-inoculation tests. The gel electrophoretic studies of all the isolates confirmed their identity as *S. sclerotiorum.*

Initial occurrence of disease was observed in second week of January. The infection persisted till late March. With the help of meteorological data the severity of stem rot of gram was correlated with that of weather conditions, mode of infection and production of apothecia in nature,

Gram was sown at different dates, viz., 15, 22, 29 October, 5, 12, 19, 26 November and 3, 10 December in 1978-79 and 1979-80. Alteration in date of sowing helped the crop to escape from disease. One hundred eleven varieties/lines of gram were screened for resistance/susceptibility against stem rot pathogen in field conditions during 1978-79 and 1979-80. Only eight lines showed less than 10% mortality.

The effect of six derivatives of thiourea hydrochloride, aqueous extracts of garlic (*Allium sativum* L.) leaf, ginger (*Zingiber officinale* Roscoe.) rhizomes, neem (*Azadirachta indica* Juss.), leaf, bark and fruit pulp and oil from neem seed was observed on the growth of *S. sclerotiorum.* Growth of the pathogen in liquid medium was inhibited by higher dosage of different plant extracts and oil from neem. However, the fungal growth was greatly reduced by comparatively lower dosage of thiourea compounds. Out of six chemicals, PTTHC was most inhibitory. Oil from neem showed maximum inhibitory effect as compared to leaf, bark, fruit pulp, garlic leaf-extract and extract from ginger rhizomes.

Each concentration of the chemical (thiourea compounds) affected pH of the medium. pH of the culture filtrate least inhibitory to the fungal growth was around 2.5 in most cases. pH increased upto 3.8 by 14th day of inoculation and the same decreased slightly after 21 days.

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Although germination of gram seeds treated with 50,000-80,000 ppm of garlic leaf-extract was delayed, it always exceeded more than 70% after four days of treatment. The germination of gram seeds was inhibited at higher concentrations of neem oil. Extracts from garlic leaf and neem oil were tested for their fungicidal value in pot culture studies. A possible role of garlic leaf-extract and oil from neem seed in controlling stem rot of gram in the field is suggested.

The effect of some thiourea compounds and systemic fungicides on ascospore germination in *S. sclerotiorum* was observed. Ascospores germinated after 10 hr at 50 ppm in RH-124, PTTHC and PCMTHC whereas they took 12 hr in the same concentration in rest of the fungicides for the same effect. PCMTHC, Bayleton, Vitavax and Plantvax were highly inhibitory at more than 300 ppm. RH-124 and PTTHC showed the same effect at 150 ppm while MCMTHC was effective at more than 500 ppm after 24 hr of inoculation.

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PLANT PHYSIOLOGY

MORPHOGENETIC STUDIES IN TISSUE AND ORGAN CULTURES OF SOME SOLASODINE-YIELDING PLANTS

Raj Nath Prasad Sup. *Dr. J. N. Singh*

A. Micropropagation and Morphogenesis in Segments of Vegetative Organs and Tissues of *Solanum* species

The main objective of the present investigation was to develop methods for clonal propagation of three medicinally important species of *Solanum*, namely, *S. surattense*, *S. laciniatum* and *S. elaeagnifolium*. Plants of all the three species of *Solanum* were established in cultures by aseptic seed germination and also by shoot tip culture in the case of *S. elaeagnifolium* as the seed germination was poor. Mainly segments of leaf, stem and root, excised from aseptically-established plants, were cultured to examine their regenerative potentiality. In some cases, other types of explants, such as, shoot apices and nodal segments were also used where segments of vegetative organs failed to give good response.

Clonal multiplication of *S. surattense* was achieved at a very fast rate (about 829,000 million plants in 1 year) by inducing direct differentiation of shoot buds from leaf-segments. The rate of multiplication was not so fast in the case of *S. laciniatum* (about 4000 million plants in 1 year) using leaf-segments, whereas it was comparatively quite slow (about 0.17 million plants in 1 year) for *S. elaeagnifolium* which was multiplied by rooting single-node stem segments.

1. Clonal Propagation

Differentiation of shoot buds without intervening callus formation was achieved from segments of leaf, stem and root of *S. surattense*, albeit the maximum number of shoot buds differentiated from leaf-segments followed by stem and root in a decreasing order. A maximum of 148 shoot buds differentiated from a leaf-segment in 30 days in an optimum treatment (2 mg/l BAP), whereas 118 and 13 shoot buds differentiated from stem and root-segments in their respective optimum treatments, i. e. 3 mg/l Kn and 3 mg/l BAP, in 45 and 30 days, respectively. Leaf-segments of *S. laciniatum* were also induced to differentiate shoot buds, but the number of shoot buds was far less than that in *S. surattense*. In an optimum treatment, i. e., 1 mg/l Kn, 39 shoot buds differentiated from a leaf-segment of *S. laciniatum* in 30 days. Segments of stem (internodal)

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and root of *S. laciniatum* could not be induced to differentiate regenerants whereas a nodal segment produced 46 off shoots in 30 days in the optimum treatment (2 mg/l Kn). There was no differentiation of shoot buds from leaf, stem (internodal) and root-segments of *S. elaeagnifolium*. However, plants of *S. elaeagnifolium* could be clonally multiplied by rooting of single-node stem segments at a slow rate. Thus, the three *Solanum* species differed greatly in their relative regenerative potentiality regarding shoot but differentiation. *S. surattense* was the most regenerative followed by *S. laciniatum*, whereas *S. elaeagnifolium* was the least.

In vitro-regenerated plantlets of all the three *Solanum* species were acclimatized in an inorganic salt solution for about 20 days before their final transplantation in soil. It took about 4 months to obtain a growing plantlet in potted soil from the time of differentiation of shoot buds from explants in culture and 3 months from rooting of nodal segments. The *in vitro*-raised plants grew normally under glasshouse conditions and appeared similar to mother plant in morphological characters. Also, they come to flowering in due course of time in the case of *S. surattense* and *S. elaeagnifolium*.

i. *Role of Growth Substances in Shoot Bud Differentiation*

The experiments conducted with different vegetative explants of *S. surattense* revealed that optimum hormonal requirement, i. e., 3 mg/l Kn for shoot bud differentiation was the same for leaf and stem, whereas root explants not only required a higher conc. of Kn, i. e. 5 mg/l, but also had an additional requirement of IAA (1 mg/l). BAP was more effective than Kn for shoot bud differentiation and 2iP the least, whereas AdS was ineffective. m-Inositol was found useful for augmenting differentiation of shoot buds; particularly in the case of root explants of *S. surattense* when used with a combination of Kn (1 to 3 mg/l) and IAA (1 mg/l). However, m-inositol when incorporated with the optimum cono. of Kn (5 mg/l) was not beneficial for root explants and it became inhibitory in the case of stem explants when used along with the optimum conc. of Kn (3 mg/l).

In leaf explants of *S. surattense*, Kn when used alone induced differentiation of shoot buds and IAA rhizogenesis. Addition of 0.1 to 1 mg/l Kn to the treatments containing 0.1 to 1 mg/l IAA inhibited rhizogenesis. But contrary to the general rule, incorporation of 0.1 to 1 mg/l IAA to 0.5 and 1 mg/l Kn progressively augmented differentiation of shoot buds commensurate with its (IAA) increasing concs. However, addition of IAA to the optimum conc. of Kn (3 mg/l) counter acted the shoot bud inducing effect of Kn. Thus, IAA played an additive role when used with suboptimal concs. of Kn.

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ii. *Role of pH and Light*

The pH 6 was found to be the optimum for differentiation of shoot buds. The pH values higher than 6 affected shoot bud differentiation more adversely than its lower values. Similarly, a maximum differentiation of shoot buds was observed under a light intensity of 2000 lux. Differentiation of shoot buds was considerably reduced under low light intensity of 300 lvx. Also, lights of different wavelengths, i. e., blue (400-530 mμ), green (460-600 mμ), red (580-700μ) and far-red (730-1000 mμ) were insufficient to produce comparable results obtained in white light.

iii. *Regulation of Morphogenesis*

Inhibitors of DNA, RNA and protein synthesis, i. e. FUdR, Act. D and cycloheximide, respectively, were employed in the experiments of cytokinin-induced shoot bud differentiation in leaf explants of *S. surattense.* Different concs. of these inhibitors were used to see their effectiveness to inhibit differentiation of shoot buds induced by incubating the explants on the morphogenetic medium (medium containing 3 mg/l Kn) for different durations before they were subjected to inhibitors' action. Among the three inhibitors used, FUdR was found to be the most effective to inhibit shoot bud differeniation followed by cycloheximide, whereas Act. D was the least. Inhibition of shoot bud differentiation by different concs. of inhibitors was directly proportional to their concs. Similarly, longer the period of incubation of explants on the morphogenetic medium before their transfer to the medium containing inhibitors, the more was the number of differentiated shoot buds. The explants incubated *ab initio* on the medium containing FUdR did not differentiate any shoot buds at the effective concs. of inhibitor.

2. Callus Culture

i. *Induction and Growth of Callus*

Callus was induced in explants of leaf, stem and root of *S. surattense.* Different concs. of auxins, such as 2, 4-D, NAA and IBA alone and in certain combinations with different concs. of Kn, were used to induce callusing in vegetative explants. Amongst the auxins, NAA (2 mg/l) was most effective followed by 2, 4-D and IBA. Auxins along with Kn were more effective than without it. Induction of callusing was more in leaf—than in stem-segment. For growth of isolated calli of leaf, stem and root, a lower conc. of auxin and cytokinin was needed than that required for induction. Hormonal requirement for maximum growth of leaf and root calli was the same, i.e., 0.5 mg/l NAA plus 1 mg/l Kn, whereas for stem callus BAP was more suitable than Kn and a higher conc. of NAA (1.5 mg/l) was required.

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ii. *Differentiation in Callus*

Calli of leaf and stem of *S. surattense*, produced in response to the treatments containing combinations of Kn plus IAA, could readily be induced to differentiate shoot buds in the presence of Kn (1.5 mg/l) and IAA (1 mg/l), whereas callus formed by a combination of NAA or 2, 4-D along with Kn could not be induced to differentiate regenerants. Similarly, callus obtained from root-segments devoid of tips could easily be induced to differentiate shoot buds, whereas callus raised from root tip explants could not be differentiated. Callus tissues from different somatio explants differed in their hormonal requirement for shoot bud differentiatiation. Leaf callus differentiated shoot buds in the presence of 1.5 mg l Kn plus 1 mg/l IAA, whereas stem callus in addition needed 100 mg/l m-inositol and root callus required not only a higher conc. of Kn, i.e., 2 mg/l, but also of m-inositol (200 mg/l) along with 1 mg/l IAA. Calli of leaf, stem and root varied in their relative regenerative potentiality in a similar way as the intact segments of these organs. Leaf callus was most regenerative followed by stem and root callus in a decreasing order. The *in vitro*-regenerated plants from calli of leaf, stem and root appeared similar in their morphological characters.

3. Histology of Shoot Bud Differentiation

Only one type of regenerant, i. e. shoot bud, was formed in different somatic explants. Shoot buds did not differentiate directly from the surface of segments of vegetative organs. Some meristematic tissue formed first followed by differentiation of shoot meristems. The meristematio tissue was like a meristemoid. Nests of tracheary elements were observed differentiating in the proximity of shoot meristems in meristemoids and they preceded shoot meristem differentiation. Generally, the tissue in the proximity of veins of leaf explants was first activated to produce meristematic tissue.

B. Androgenesis

Anthers of three developmental stages, i.e., (i) containing most of the pollen grains in tetrads, (ii) containing isolated pollen grains with thin exine and (iii) containing pollen grains with thicker exine were employed to induce androgenesis. Amongst the anthers of three stages, the anthers of the first stage responded favourably. Generally, they remained more green than the anthers of second stage, whereas those of the third stage mostly turned brown. Differentiation of few shoot buds associated with callusing from the anthers of the first stage was observed on Nitsch and Nitsch (1969) medium supplemented with 0.1 mg/l BAP, 25 mg/l AdS and 1500

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mg/l m-inositol. The androgenic callus along with differentiating shoot buds required Kn (2 mg/l) plus a low conc. of NAA (0.025 mg/l) supplemented to the Murashige and Skoog (1962) medium for further multiplication and development of shoots. All the androgenio plants were found to be tetraploids (4n = 48) and differed with the normal diploid plant mainly in lacking spines, having smaller ovate leaves, tender stem and sprawling habit. The *in vitro*-raised androgenic plants grew well in potted soil and also flowered.

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SOIL SCIENCE AND AGRICULTURAL CHEMISTRY

STUDIES ON THE EFFECT OF COPPER AND ZINC APPLICATION ON PADDY

H. P. Agrawal Sup. *Dr. M. L. Gupta*

Copper and zinc, two of the several essential plant micronutrients, are responsible for a large number of metabolic functions in the plant system. A deficiency of copper results in the withering of the tips without spotting or marked chlorosis where as zinc deficiency causes whitening of the young leaf blades. first at the base and then at the veins, followed by the appearance of brown spots on the old leaf blades (Ishizuka and Tanaka, 1962). Their, deficiency results in the non-utilization of other plant nutrients, some times resulting in their accumulation as well as the accumulation of undesirable metabolites ultimately inviting the plant pathogens and predators to enjoy on the weak plant. Paddy is cultivated almost throughout the year and generally under flooded conditions. Flooding of the soil introduces a variety of changes in the nutriention composition of the soil. Decreased availability of Cu and Zn in rice soils is also a consequence of flooding (Ponnamperuma, 1977). Under conditions of limited availability of Cu and Zn, the success of rice cultivation depends upon the creation of adequate concentrations of the two elements in the soil so that the nutrient composition of the plants is also suitably modified, resulting in fuller utilization of other plant nutrients.

This experiment was undertaken to study the effects of Cu and Zn application on paddy in a Gangetic alluvium soil, poor in both Cu and Zn. To examine, various aspects, field. experiments were conducted during the year 1981 and 1982, at the Research Farm of the Institute of Agricultural Sciences, Banaras Hindu University. Copper and zinc were added @ O, 10, 20, 40 kg. ha^{-1} as $CuSO_4$ or $ZnSO_4$, respectively in all possible combinations. The observations were recorded, with respect to dry matter production and concentration and uptake of nutrients at maximum tillering stage, full heading stage and at harvest, in the grain and in the straw. Protein and starch content of the grain was determined to assess the effects on the grain quality. Standard and well accepted procedures were used for the chemical analysis of the plant and soil samples.

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A highly significant increase in the dry matter production due to the application of Cu and Zn was observed at all the stages. Generally, Zn levels were superior than Cu levels. Application of 40 kg. Zn ha^{-1} and 20 kg. Cu ha^{-1} increased the grain yield by about 70-80 percent over control. Copper and zinc interact at various levels, especially higher levels of each. Copper at 40 kg. ha^{-1} decreased the grain yield. $Cu_{20}Zn_{40}$ treatment produced about 8 tons ha^{-1} of gross crop produce.

Copper and zinc application also resulted in the increased concentrations of N, Zn and Cu in the rice plants at various stages. Contents of K were generally not affected, except in the rice straw whereas those of P, Fe and Mn were generally decreased. A significant interaction effect of Cu and Zn on the concentration of nutrients was observed. Increase in nitrogen content was more, generally, due to Cu levels whereas Zn had more effect in decreasing the P content.

Copper and Zn contents of the rice plant increased 2-4 times due to their application. Cu_{40} tended to decrease the Zn content whereas Zn_{40} decreased the Cu content. Generally Cu had more effect in decreasing the Zn content.

Iron and manganese contents of the plants were decreased only at the 10 kg. levels of each and the other higher levels did not have any significant decreasing effeet.

Rice plants contained maximum N, P, K, Zn and Cu at maximum tillering stage. Maximum Fe was found in the straw, whereas the Mn content of the rice straw and the rice plants at full heading stage were similar. Rice straw contained minimum amounts of N, P, Cu and Zn whereas, an accumulation of these and also of P, was observed in the grain. Rice grain contained much less K, Fe and Mn than that was present in the rice straw.

Uptake of plant nutrients, being a result of nutrient concentration and dry matter production, increased at all the stages due to the application of Cu and Zn. The maximum gross yield of 9.3 tons ha^{-1} produced by the treatment $Cu_{20}Zn_{40}$ removed 118 kg. N, 15.7 kg. P, 92.6 kg. K, 96.8 g. Cu, 406 g. Zn, 1016 g. Fe and 1147 g. Mn.

Protein content of the grain was increased by 6-8 percent whereas starch content was not affected.

It was concluded that 10-20 kg. Cu ha^{-1} alongwith 20-40 kg. Zn ha^{-1} may be expected to provide satisfactory farm output in such soils.

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STUDIES ON SOLUBILIZATION AND AVAILABILITY OF PHOSPHORUS FROM ROCK PHOSPHATES IN SOIL

Rajendra Rai Sup. *Dr. Sant Singh*

Direct application of rock phosphate in soil has gained increasing acceptance by agricultural scientists of the world. However, the consensus has been that rock phosphates are not suitable, in comparison to water soluble fertilizers particularly, in neutral and calcareous soils. After the geological findings of its low grade deposits in India, an urgent need for the variety of methods and practical solutions have generated a demand for information on all aspects of the behaviour of rock phosphates in soil.

To evaluate the relative efficacies of Mussoorie rock phosphate, Purulia rock phosphate and Jordan rock phosphate in combination with pyrites in respect of their crop response and phosphorus uptake in waterlogged paddy, variety Ratna field experiments in two seasons were conducted in Sindri soil having pH 8.0 and $CaCO_3$ 7.0%. It was found that rock phosphates without pyrites application were of little use and superphosphate was found to be most effective fertilizer. Application of rock phosphate with pyrites (2.5t/ha) to the soil was highly beneficial in augmenting the quantitative increase in yield of the crop. Phosphorus uptake by the crop was also increased due to application of pyrites. The efficiency of rock phosphates further increased with higher dose of pyrites (5.0 t/ha) application. Of the three rock phosphates studied, Mussoorie rock phosphate showed highest degree of efficiency due to higher initial solubility and its chemical nature as carbonateapatite. Jordan rock phosphate was akin to Mussoorie rock phosphate which might be due to softness and less sesquioxide content in the rock. Purulia rock phosphate showed lower performance in comparison to other two rock phosphates due to likely substitution of phosphate with fluorine and presence of iron and aluminium oxides in greater proportion (>17%).

The residual effects of different rock phosphates were also studied on two successive crops—wheat and paddy. The induced beneficial effects of pyrites in the first year could not produce any significant increase in yield of individual crop. Nevertheless, rock phosphates in general, evinced greater residual effect than superphosphate. The relative efficiency of rock phosphates in respect of grain and straw yields varied in the order : Mussoorie rock phosphate ≥ Jordan rock phosphate > Purulia rock phosphate. Application of pyrites in the soil did not produce any comparable difference in yield values in second residual crop also.

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Mussoorie rock phosphate performed better than superphosphate and Jordan rock phosphate in the second residual crop—paddy. Rock phosphates with high level of pyrites outyielded superphosphate no pyrites treatment. Attainment of equilibrium in soil pH with the increase in time and fixation of phosphorus in presence of higher amounts of iron from pyrites might be responsible for such behaviour of rock phosphates in presence of pyrites in the residual crops. Similarly, cumulative data of the three crops—paddy, wheat, paddy—showed the following trend in performance of different phosphatic fertilizers : Mussoorie rock phosphate > Jordan rock phosphate > superphosphate > Purulia rock phosphate at higher dose of phosphorus (120 kg P_2O_5/ha) with higher level of pyrites (5.0 t/ha).

Incubation studies, using ion exchange technique, of rock phosphates and superphosphate in soil with different levels of pyrites (0.0, 2.5 and 5.0 t/ha) under submerged condition showed highest release of phosphorus in superphosphate treatment, followed by Mussoorie rock phosphate, Purulia rock phosphate and control in descending order. Release of phosphorus from native soil increased with the first level of pyrites (2.5 t/ha) application followed by decrease at second level (5.0 t/ha). Phosphorus release decreased in superphosphate with the application of pyrites which is more prominent at the second level. Increased solubilization of rock phosphate due to pyrites was observed for Mussoorie rock phosphate only. Such increase for Jordan and Purulia rock phosphates was negligible.

In another laboratory experiment, release of phosphorus from the three rock phosphates by charging them with seven organic acids. viz., acetic, oxalic, lactic, citric, fulvic, hymatomelanic and humic acids varying in molecular weights and exhibiting different behaviour was also studied. Remarkable effects of different organic acids on weathering of rock phosphates have been observed. Significant amounts of phosphorus were released by all the organic acids (0.1%) from all the rock phosphates due to formation of Werner-type complex ions of the organic anions with Ca^{++}, thus dissolving rock phosphates by lowering the calcium activity.

Irrespective of nature and type of organic acids, highest release in phosphorus has been observed with Purulia rock phosphate followed by Mussoorie and Jordan rock phosphates in a descending order. The trend is related to the origin, age and chemical composition of rock phosphates.

Irrespective of types of rock phosphates, various monomers show the following trend in solubilization in a descending order :

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Oxalic acid > Citric acid > Acetic acid > Lactic acid. The solubilizing effects, however, are related to the number of carboxylic and hydroxyl groups present in acids.

Solubilizing effects of different organic macromolecules followed the following trend :

Fulvic acid > Hymatomelanic acid > Humic acid, which is the trend in molecular weight of the acids in ascending order. Solubilization effects of all the organic acids decreased with dilution (0.01%).

After being weathered by various organic acids, all the rock phosphates have shown remarkable increase in phosphorus availability which, however, is most prominent for Purulia rock phosphate and Jordan rock phosphate with all the organic macromolecules, suggesting the likely beneficiation of rock phosphate by organic matter on one hand and its likely increased efficiency for crop yield on the other.

The importance of these investigations is clearly reflected from the findings that the efficiency of indigenous rock phosphates can be profitably enhanced with the addition of pyrites and organic matter. Particularly, Mussoorie rock phosphate in combination with pyrites can be effectively utilized while the Purulia rock phosphate, due to absence of free calcite content, can be better utilized in the presence of organic matter.

STUDIES ON INTERACTIONS OF NITROGEN, PHOSPHORUS AND ZINC IN WHEAT CROP

Ravindra Narayan Singh Sup. *Dr. Bharat Singh*

The high yielding crop varieties especially of wheat which were introduced in the country from 1965-66 onwards are now being largely grown by the farmers. The requirement for plant nutrients of the new high yielding varieties as compared to the previous low yielding varieties is almost double, for exploiting the full yield potentials. In the early years of the cultivation of new varieties only the deficiency of nitrogen was encountered. After two to three years, is was found that not only nitrogen but also phosphorus deficiency became a limiting factor in determining the yield. The optimum yield levels were afterwards largely achieved through balanced application of both N and P as well as other major and micronutrients.

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There is considerable literature concerning the nutrition of N, P and Zn on several wheat varieties but there is very little information regarding the interactions among the above nutrients on the crop. Keeping in view the prospects of the production of wheat var. HUW-12, field experiments were conducted in farmer fields during rabi seasons of 1980 and 1981 to obtain information regarding the individual and the interaction effects of N, P and Zn treatments on the yield and yield bearing parameters of different stages of crop growth. Besides, the content and uptake of N, P, K and Zn in drymatter and grain were assessed. Furthermore, the availability of N, P and Zn is the post harvest soil was also evaluated.

The experiment was laid in Factorial Randomized Block Design with treatments consisting of three levels each of N, P and Zn and their combinations. The treatments were replicated three times. An uniform basal dressing of potash as potassium chloride was applied.

The various soil and plant analyses were done by usual conventional methods as well as modern precision instrumental methods, e. g., atomic absorption spectrophotometry, colorimetry and flame photometry. The data obtained were analysed statistically and discussed to draw valid conclusions.

The N and P treatments individually produced significant increase in the plant height, number of tillers and dry matter yield at all the growth stages and also in grain yield of wheat in both the years. However, the treatment of Zn was nonsignificant in this respect. Only the lower level of Zn proved positive in effect. The N_{120}, P_{60} and Zn_{20} treatment levels gave individually greater plant height and number of tillers and also dry matter and grain yields, Of them, N_{120} treatment produced maximum of all the above parameters. Among various interactions, only N x P interaction was significantly effective on growth and yield parameters in both the years.

The increase in the lodging of the crop with increasing N levels was reduced with increasing phosphorus application in both the years. Minimum lodging with greater plant height and number of tillers, grain yield and dry matter at all the growth stages and were recorded with N_{120} x P_{60} x Zn_{20} treatment combination in both the years.

In general, the N content was significantly affected by all the treatments of N and P separately in plant at all the growth stages and also in grain in both the years. But Zn treatment was nonsignificant in this respect. Increasing levels of N increased the N content while it was decreased with increasing level of P application. However, the N concentration

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in plant and grain was not in linear trend with Zn levels. Only N x P interaction was significantly effective on N content in plant and in grain at second stage during the second year. Among all, N_{120} x P_0 x Zn_0 combination induced highest N concentration in both plant and grain in both the years.

Significant enhancement in N uptake by plant at all the growth stages and also in grain was found with increasing levels of N and P individually but, Zn treatment gave non-significant increase in both the years except at second stage during second year. Higher u ptake of nitrogen in plant at all the growth stages and also in grain was observed with N_{120}, P_{60} and Zn_{20} levels in both the years. Among them, the maximum uptake was found with N_{120} treatment. Among the interactions, only N x P was significantly effective in this respect. However, higher uptake of N was recorded N_{120} x P_{60} x Zn_{20} followed by N_{120} x P_{60} treatment combination.

The individual treatments of N and P significantly affected the P concentiation at all the growth stages in plant and in grain in both the years except P treatment at the harvest stage in the first year. Phosphorus concentration in plant and grain was significantly increased with increasing levels of P treatment. But the reverse was noted with increasing levels of N in both the years. Only the lower dose of Zn was positively effective in this respect. Higher P content was recorded with N_0, P_{60} and Zn_{20} levels separately. Among them, P_{60} level at the first stage and N_0 level at the second stage and harvest stage in plant and grain were responsible for maximum P concentration in both the years. Only N x P interaction was significantly effective on P concentration in plant at all the growth stages and in grain except in plant at second stage in the first year and the harvest stage in the second year. The N_{60} x P_{60} combination at first stage and $N_0 \times P_{60}$ at rest of the stages of plant and in grain induced highest P concentration in both the years.

The uptake of P was significantly increased with increasing levels to N and P at all the growth stages in plant and in grain in both the years. However, the P uptake enhanced with only lower dose of zinc. The maximum uptake of P was obtained with P_{60} level at the initial stage and N_{120} level at the second and harvest stages of plant and in grain in both the years. Only N x P interaction was significantly effective in this respect. However, the maximum uptake was observed with N_{120} x P_{60} x Zn_{20} treatment combination.

The Zn concentration was significantly decreased with increasing levels of N and P treatments at all the growth stages in plant and in grain in both the years. The Zn treatment was positively significant in this res-

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pect. No treatment interaction was significantly effective on plant Zn content in any of the years. However, N_0 x P_0 x Zn_{40} treatment combination at all the growth stages in both the years and P_0 x Zn_{40} at second stage during the second year induced highest Zn concentration in plant. Zn concentration in plant. Zn concentration in grain was significantly affected by N x P and P x Zn interactions in both the years and the highest concentration being with P_0 x Zn_{40} treatment combination.

The uptake of Zn in plant throughout its growth and also in grain was significantly increased with increasing levels of N and Zn but it decreased with increasing rates of phosphorus in both the years. Interaction effects of N x P and N x Zn were also significant in this respect. However, the maximum uptake of Zn was observed with N_{120} x P_{30} x Zn_{40} treatment combination.

The K concentration in plant was significantly affected by N treatment only at the harvest stage in the first year and at the second and harvest stages in the second year. It increased with increasing levels of nitrogen during first year while in the second year N treatment had no linear impact. The P treatment was significantly effective only at initial stage in the first year and at the second and harvest stages in the second year. Only the lower level of Zn enhanced the K concentration in plant at all the growth stages in both the years. All the treatment interactions were nonsignificantly effective in this respect except the N x P interaction at second and harvest stages during the second year. Concentration of K in grain was significantly affected by N and P treatments in both the years while Zn treatment was significantly effective only in the second year. Its concentration in grain was suppressed with increasing level of N in both the years. N_0, P_{30} and Zn_{20} treatment levels individually gave higher K concentration. Only P x Zn treatment interaction was significantly effective on K concentration of grain in second year.

The uptake of K was significantly affected by the treatments of N and P separately in plant at the growth stages in both the years. But the treatment of Zn was effective only at initial stage in the first year and the second and harvest stages in the second year. The uptake of K increased with increasing levels of N and P. While lower level of Zn had positive effect in this respect. Only N x P interaction was significantly effective on the uptake of K by plant at all the growth stages in both the years. The uptake of K by grain was significantly affected by N treatments in both the years and by P and Zn treatments only in the second year. Among them, N_{120} level gave the maximum K uptake in both the years. Among interactions, only N x P was significantly effective on K uptake by grain during second year and N_{120} x P_{60} combination gave the maximum uptake.

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Availability of N in the post harvest soil was significantly affected by N and P treatments separately in both the years. The available N increased with increasing levels of N treatment but decreased with increasing levels of P treatment. Among interactions, only N x P significantly affected the N availability in the first year and $P_0 \times N_{120}$ combination induced the maximum effect.

All the individual treatments of N, P and Zn significantly affected the availability of P in the post harvest soil in both the years. The availability of P increased with increase in P levels while it decreased with increasing levels of N and Zn treatments. Among them highest P availability was noted with P_{60} level in both the years. Among interactions, only N x P was significantly effective and the combination $N_0 \times P_{60}$ gave the maximum availability of P in both the years.

Only Zn treatment in first year and all the individual treatments of N, P and Zn in second year were significantly effective on Zn availability in the post harvest soil. The availability of Zn increased with increase in Zn levels while it decreased with increasing levels of N and P in both the years. None of the treatment interaction was significant in this respect.

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FACULTY OF ENGINEERING & TECHNOLOGY

APPLIED CHEMISTRY

STUDIES ON THE CHEMISTRY OF URANIUM AND RELATED CATIONS

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The investigations presented in this thesis were undertaken in March 1980 and continued till date. The work reported in the thesis submitted by the author has been divided into two parts A and B according to the two distinct class of investigations undertaken. Thus the part A (Chapter 1-4) deals with separation techniques specially for U (VI) and Th (IV); one of these is the solvent extraction and the other is chromatography. The part B is devoted to the synthetic and structural studies of mixed ligand complexes of uranium (VI) with phenylacetic and lactic acid as primary ligands and various amines as the secondary ligands.

Chapter one of this thesis gives a brief and general treatment of the solvent extraction and chromatography in analytical chemistry. A critical discussion of the salient and relevant features of the various solvent extraction systems and in particular paper chromatography (PC), thin layer chromatography (TLC), and reverse phase extraction chromatography (RPEC) have been incorporated with special emphasis to the extraction and separation of uranium (VI) and thorium (IV) from other elements.

Chapter two and three contain the results obtained for the extraction of U(VI) and Th(IV) from aqueous nitric acid solutions respectively under different experimental conditions by using a new solvent tri-iso-amylphosphate (TAP) prepared from fusel oil a by-product of Indian-Alcohol Industry.

Thus it has been found that 20% TAP is sufficient to extract 95% of U(VI) in concentrations as low as 1×10^{-4}M. It has also been ascertained that considerable co-extraction of nitric acid takes place along with the U(VI) extraction but the amount of acid extracted continuously diminishes with increasing U(VI) extraction. Eventually, at $[HNO_3]_a = 3.0N$ gives maximum extraction when all the extracted by TAP was gradually replaced

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by the U(VI) and a disolvated species is formed in the organic phase. Hence the following mechanism of extraction is proposed :

$$2[TAP.HNO_3]_0 + UO_2(NO_3)_2 \rightarrow [UO_2(NO_3)_2.2TAP]_0 + 2HNO_3$$

Further, the presence of 1.0M $NaNO_3$ as salting out agent was found effective only at lower acidities. Thus 98% of U(VI) is extracted by the 20% TAP at 0.5 N [HNO_3] and 1.0M [$NaNO_3$]. Extraction was also found increasing gradually with increasing U(VI) concentration upto 3.6×10^{-4}M. Under optimum condition separation of U(VI) from various other metal ions was investigated and it was found that while the presence of equivalent amount of cations such as Ca^{2+}, Ba^{2+}. Sr^{2+}, Mg^{2+}, Pd(II) etc. does not interfere with the U(VI) extraction, but some other cations eg. Ce(IV), Th(IV), Nb(V) etc. are coextracted. It is also revealed that when TAP was diluted with non polar diluents like carbon tetrachloride or kerosene higher values of distribution ratios were obtained under optimum conditions as compared to those when a polar diluent viz. chloroform is employed.

Chapter three describes the results obtained for the extraction of thorium (IV) nitrate from aqueous nitric acid solution by diluted TAP (CCl_4). With increasing initial aqueous acidity the extraction of thorium (IV) increases gradually although the co-extraction of nitric acid also increases. Nevertheless, the acid extracted in the organic phase has always been found to be less in the presence of Th(IV) than in its absence. Hence, the optimum extraction of 94% of Th(IV) was achieved by 55% TAP at [HNO_3]=5.0N, when the concentration of the metal itself is as low as 2.0×10^{5}M. A tri-solvated species is formed in the organic phase and the mechanism of extraction is proposed as :

$$Th(NO_3)_4 + 3\ [TAP.HNO_3]_0 \rightarrow [Th(NO_3)_4.3TAP]_0 + 3HNO_3$$

An interesting feature of this investigation is that thorium nitrate can also be extracted quatitatively in the pH range of 4.06-4.5 by much more diluted i. e. only 20% TAP in CCl_4. In this case the log CTAP vs log D plot gave a straight line with slope of nearly two and consequently the formation of a disolvated species was established in the organic phase while the mechanism of the extraction is represented as :

$$2[TAP.H_2O]_0 + Th(NO_3)_4 \rightarrow [Th(NO_3)_4.2TAP]_0 + 2H_2O.$$

Presence of salting out agent was tested at pH 4.06 and it was found that in presence of 1.0M $NaNO_3$, 99.9% extraction of thorium nitrate would be achieved by still more dilute TAP i. e., only 18% in CCl_4. Once again the extraction was found increasing in direct proportion to the metal

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concentration i. e., upto $[Th(IV)] = 2.6 \times 10^{-5}$ at $[HNO_3] = 5.0N$ and 3.2×10^{-3} M at pH 4.06. Carbon tetrachloride was found to be better than other polar and non-polar diluents. It is also shown that extraction of Th(IV) performed at pH 4.06 enables its quantitative separation from the equivalent amount of various other cations viz. Li^+, Na^+, Mn(II), Sr (II), Zn(II), Ag(I) etc. while percentage recovery of Th(IV) was affected to some extent by the presence of Eu(III), Zr(IV), Hf(IV), In(III) etc. due to their co-extraction.

In chapter four, as mentioned, two different categories of chromatographic processes have been employed, viz.

A. Classical or the usual method,

B. Reverse phase extraction chromatographic method (RPEC).

In chapter five an introduction to the Part B of this thesis describing the synthetic and structural studies on the complexes of U (VI) has been given. A critical discussion of the significant physico-chemical techniques such as molar conductance and magnetic susceptibility measurements and the infrared and electronic spectral studies used for the characterisation of unknown compounds and mixed ligand complexes has been given.

Chapter six comprises the results on the interaction of uranyl-bis-phenyl acetate with a number of bidentate and mono dentate heterocyclic amines as well as many simple amines yielding sixteen hitherto unreported isolable mixed ligand complexes. All these complexes which separate as powders or crystalline solids are characterised by their colour, melting point, elemental analysis, infrared and electronic spectral data.

The very low values of molar conductance ($<50 cm^{-2}. ohm^{-1}. mole^{-1}$) in dimethlyl formamide reveal that these compounds are non-electrolyte in nature; the significantly low values of magnetic susceptibilities (50-110 $\times 10^{-6}$ c. g. s. units) confirm their diamagnetic nature.

The mixed ligand complexes prepared show a strong absorption band in the region 1000-900 cm^{-1} due to the asymmetric atretching mode υ_3 of UO_2 group. The O-U-O bending mode has been identified in the range 200-250 cm^{-1}. For a linear symmetric structure υ_1 is forbidden hence not observed.

In the primary complex, uranyl bis-phenyl acetate two strong bands namely $\upsilon_{asym}C00^-$ and $\upsilon_{sym}\ C00^-$ were clearly identified at $1510 cm^{-1}$ and $1400 cm^{-1}$ respectively. The difference in the position of the two bands in this case is $110 cm^{-1}$ which is characteristic for the bidentate nature of the phenyl acetate group. This bidentate nature of the phenyl acetate group has been found to be maintained in all the mixed ligand complexes.

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The bonding of the secondary ligand i. e. the amines is shown by the lowering in the (N-H) stretching frequency in the 3400-3100 cm^{-1} region of the free ligand e. g. ethylene diamine, o-phenylene diamine, diethyl amine and dimethyl aniline. This indicates definite coordination to the metal through the nitrogen atom of the amino groups which is further supported by the negative shift in (C-N) stretching frequency of the ligands on complexation.

However, the bonding of the heterocyclic amines by coordination through nitrogen to the uranyl phenyl acetate primary complex is evidenced by the alteration in the ring vibrations (1600-1400 cm^{-1}) and (C-H) out of plane deformation or ring deformation modes in the free ligands. Thus, a band for δ (C-H) mode was observed at 720 cm^{-1} for pyridine, 755-800cm^{-1} for picolines and at 748 cm^{-1} and 795 cm^{-1} for quinoline and iso-quinoline complexes. Intense bands at 739 and 755 cm^{-1} in bidentate heterocyclic amine complexes were found considerably shifted towards lower frequency values than their respective positions in the original ligands. Ultimately, formation of mixed-ligand complexes was confirmed in all the cases by the identification of metal nitrogen bands appearing in the region 250-300-^{1}.

Due to the comparable magnitude of the ligand field splitting and spin-orbit coupling the electronic spectra of uranyl ion is exceedingly complicated. Thus a band envelop centered around 24000 cm^{-1} is attributed mainly to the uranyl moiety and its intensity remains more or less unaltered on complexation. Nevertheless, few bands in the 33500-42500 cm^{-1} region may be assigned as ligand bands attributed to $\pi \longrightarrow \pi^*$ or $n \longrightarrow \pi^*$ transitions.

The synthetic and structural studies on another series of sixteen new mixed ligand complexes of uranyl lactate with the same nitrogen donors as used for uranyl bis-phenyl acetate have been described in chapter seven. These complexes were also characterised by their melting point, elemental analysis and magnetic data together with their infrared and electronic spectral studies. Conductance measurements could not be made for these compounds since all of these were insoluble in organic solvents including dimethyl formamide. Presence of water in these complexes has been established by thermal studies as well as by the characterisation of specific bands viz. υ(0-H), $\rho_r(H_2O)$ and υ (M-0) in the infrared spectra of the complexes.

Uranyl bands were observed at $\approx$ 900 cm^{-1} and 220-260 cm^{-1} as υ_3 and υ_2 modes. Absence of a band at 830 cm^{-1} due to υ_1 mode shows that linearity of the O-U-O group is maintained in all the secondary complexes as well as in the primary complex uranyl lactate.

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Bidentate nature of lactic acid was established by the splitting of the carboxylate band into two bands at 1550 cm^{-1} ($\upsilon_{asym}COO^-$) and 1400 cm^{-1} ($\upsilon_{sym}COO^-$) and also a few more bands of medium to sharp intensity in the region 1150 and 1020 cm^{-1} due to υ(C O) and δ (O-H) modes of secondary alcohols.

Mixed ligand complexes with simple amines show υ (N-H) bands in the region 3340-3350 cm^{-1} and also at $\approx$3250 cm^{-1}. The υ(C-N) has been observed at $\approx$1070 and 1120 cm^{-1} which are significantly shifted (negative) from their position in the ligand.

The most informative region for the bonding of mono and bi-dentate heterocyclic amines is the one where ring deformation modes occur. Thus a positive shift of $\approx$ 10 cm^{-1} in the complexes affirms coordination through the nitrogen of the pyridine ring. Further, the bands observed in the region $\approx$1600 cm^{-1} to 1400 cm^{-1} which are characteristic of ring breathing frequencies of aromatic compounds also substantiate complexation through the ring nitrogen.

The υ (M-N) vibrations for this series of complexes have also been identified in the region 220-300 cm^{-1}. Electronic spectral measurements were also made for few representative compounds and the results similar to those described above for the uranyl-bis-peenyl acetate complexes.

STUDIES IN THE CHEMISTRY OF NITROGEN AND SULPHUR COMPOUNDS

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Arun Kumar Pandey

The following is a brief outline of the work presented in this thesis. The thesis is divided into two parts. *Part-I* deals with the studies in oxidative dealkylation of 2-S-alkylisobiurets (where alkyl = benzyl or allyl groups) followed by cyclisation into sulphur and nitrogen heterocyclic compounds as described below. *Part-II* deseribes experiments on the preparation of 1-formamidino/arylamidinosubstituted-2-S-benzylisothiocarbamides and their oxidative debenzylation and cyclisation into the corresponding 1,2,4-thiadiazolidines.

Part-I

This part is divided into four sections : In Section-1 are described the preparation of various 1-, 1,5-, 1,1,5- and 1,3,5-substituted-2/4-S-benzylisobiurets and 1,5-disubstituted-2-S-allylisobiurets required for oxidation

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studies. These compounds are obtained by the condensation of appropriate N and S substituted isothiocarbamides with phenylisocyanate.

Section 1

This is an account of the oxidation studies of the isobiurets described in Section-1 with bromine or iodine in chloroform. Only bromine has been found to debenzylate the S benzylisobiurets and cyclise them into the related 1,2,4-thiadiazolidines/thiadiazolines. The dislodgement of allyl group of S-allylisobiurets and their cyclisation into the corresponding 1,2,4-thiadiazolidines can, however, be effected only by iodine.

The ethanolic ammoniacal hydrogen sulphide/or pyridinetriethylamine hydrogen sulphide reduction of the above oxidation products of thiadiazolidines and thiadiazolines resulted in the formation of the corresponding 2-thiobiurets.

The methyl- and ethyl groups in 1,5-diphenyl-2-S-methylisobiuret and 1,5-diphenyl-2-S-ethylisobiuret refferred to above could not be removed in a like manner.

Oxidation in chloroform/benzene medium

Oxidation of 1-substituted-4-S-benzylisobiuret (I) : Formation of 5-imino-3-oxo-2-phenyl-1,2,4-thiadiazolidine (VI).

The oxidation of 1-substituted-4-S-benzylisobiuret (described in Section-1) with bromine in chloroform afforded the related 1,2,4-thiadiazolidine (VI).

Oxidation of 1,5-disubstituted-2-S-benzylisobiurets (II) : Formation of 5-substitutedimino-3-oxo-2-phenyl-1,2,4-thiadiazolidines (VII).

These isobiurets (V) also on oxidation with iodine in boiling chloroform/benzene afforded the related 1,2,4-thiadiazolidines (X).

Reduction of 1,2,4-*thiadiazolidines/thiadiazolines listed above :*

5-imino-3-oxo-2-phenyl-1,2,4-thiadiozolidine (VI) and 5-arylimino-3-oxo-2-phenyl-1,2,4-thiadiazolidines (VII) described earlier, on reduction with ethanolic ammoniacal hydrogen sulphide afforded the corresponding 1-substituted-4-thiobiuret (XI) and 1,5-disubstituted-2-thiobiurets (XII).

5-Disubstitutedamino-3-oxo-2-phenyl-1,2,4-thiadiazolines (VIII) and 5-arylimino-4-aryl-3-oxo-2-phenyl-1,2,4-thiadiazolidines (IX) on reduction with hydrogen sulphide in pyridine-triethylamine solution afforded the corresponding 1,1,5-trisubstituted-(XIII) and 1,3,5-trisubstituted-2-thiobiurets (XIV) respectively.

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Section 2

This section incorporates the preparation of 1-substituted-, 1,5-disubstituted-, 1,1,5-trisubstituted-and 1,3,5-trisubstute l-2-thiobiurets by already known methods of reductive debenzylation/deallylation of related S-benzyl/S-allyl isobiurets in ethanolic ammoniacal hydrogen sulphide and pyridine· triethylamine and hydrogen sulphide and their oxidation with bromine in cold dilute ethanol to the corresponding 1,2,4-thiadiazolidines/thiadiazolines.

These compounds were prepared for characterisation of the products obtained in earlier experiments. A short discussion of the results and a probable mechanism has been proposed for the oxidative debenzylation in isobiuret systems in Section 4.

Part—II

Part II comprises of four sections : **Section-1** deals with a brief review of the methods of preparation of formamidino-thiocarbamides to serve as back ground for the present study and is a record of the experimental work of the preparation of 1-formamidino-3-aryl. (XV), 1-p-tolylamidino-3-aryl-(XVI), and 1-(N,N'-diarylamidino)-3-arylthiocarbamides (XVII) by the interaction of appropriate substituted guanidines and arylisothiocyanates. These XV, XVI, and XVII on benzylation afforded the corresponding 1-formamidino-3-aryl-(XVIII), 1-p-tolylamidino-3-aryl-(XIX) and 1-(N, N'-diarylamidino)-3-aryl-2-S-benzylisothiocarbamides (XX).

Section 2

This is a description of the oxidation of the formamidino/substituted-amidino-isothiocarbamides (XVIII, XIX and XX) described in Section-1. Only bromine has been found to debenzylate these S-benzylisothiocarbamides and cyclise them into the related 1, 2, 4-thiadiazolidines.

Section 3

(i) This is an account of the preparation of the authentic samples of substituted-1, 2, 4-thiadiazolidines by the oxidation of formamidino/substitutedamidino thiocarbamides (XV, XVI, XVII) described in Section 1. These were required for characterisation of the compounds described in Section 1 and 2.

1-Formamidino-3-aryl-(XV), 1-p-tolylamidino-3-aryl-(XVI) and 1-(N, N'-diarylamidino)-3-aryl-thiocarbamides (XVII) were oxidised in dilute ethanol with bromine to the corresponding 5-substitutedimino-3-imino-(XXI), 5-substitutedimino-3-substitutedimino-(XXII) and 5-substitutedimino 3-substitutedimino-2-substituted-1, 2, 4-thiadiazolidines (XXIII).

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Oxidation of 1-formamidino-3-arylthiocarbamides (XV) : Formation of 5-substitutedimino-3-imino-1, 2, 4-thiadiazolidines (XXI).

(ii) Ethanolic ammoniacal hydrogen sulphide reduction of thiadiazolidines described in Section-3.

5-Substituted-imino-3-imino-, 5-substitutedimino-3-substitutedimino- and 5-substitutedimino-3-substitutedimino-2-substituted-1, 2, 4-thiadiazolidines described in Section-3 on reduction with ethanolic ammoniacal hydrogen sulphide afforded the corresponding 1-formamidino-3-aryl-, 1-p-tolylamidino-3-aryl- and 1-(N, N'-diaryl-amidino)-3-arylthiocarbamides respectively.

A probable mechanism for oxidative debenzylation of isothiocarbamide into corresponding 1, 2, 4-thiadiazolidine has been described in Section-4.

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APPLIED MATHEMATICS

SOME ASPECTS OF THERMAL AND MASS DIFFUSION ON MHD FLOWS

Raj Nath Sup. *Dr. H. L. Agrawal*

This thesis consists of six chapters. In first chapter which is introductory, a brief survey of the results obtained by various authors during their investigations have been made and their relations to the present work have also been shown.

In second, chapter an investigation of unsteady flow of a visco-elastic (Oldroyd) fluid past an infinite plate in the presence of transverse magnetic field under the following conditions (i) suction velocity normal to the plate oscillates in magnitude about a constant non-zero mean and (ii) free-stream velocity oscillates in time about a constant mean, has been made. The effects of magnetic field and suction velocity on mean velocity, amplitude and the phase of skin-friction have been shown graphically followed by a discussion. Mean skin-friction for different parameters has been entered in a table. It is found that the increase of magnetic field increases mean velocity and amplitude of skin-friction and decreases the phase of skin-friction. A comparative study of the flow phenomenon for Newtonian and non-Newtonian fluids has been made.

In third, chapter the natural convection flow of an incompressible visco-elastic fluid (Walter's liquid B') past an infinite porous vertical plate has been discussed under the conditions : (i) suction velocity normal to the plate oscillates in magnitude about a constant non-zero mean, and (ii) convection is produced by interaction of force of gravity and density differences caused by simultaneous diffusion of thermal energy and chemical species. The effects of Schmidt number S_c, Grashof number, G_1, modified Grashof number G_2 and suction parameter A on mean velocity for Newtonian and non-Newtonian fluids have been discussed for heating ($G_1 < 0$) and cooling ($G_1 > 0$) of the plate by free convection currents. The variation of the amplitude and the phase of skin-friction for different parameters have been enterpreted graphically.

In fourth, chapter an analytical study has been performed to examine the heat and mass transfer characteristics of natural convection flow of an incompressible visco-elastic fluid past an infinite vertical plate

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under the combined buoyancy effects of thermal and mass diffusion in the slip flow regime. The problem has been solved for velocity, temperature and concentration fields. Mean velocity for Newtonian and non-Newtonian fluids for rarefied and non-rarefied states have been discussed graphically followed by a discussion. The mean skin-friction for different values of parameters have been tabulated.

In fifth, chapter an analysis for combined buoyancy effects of thermal and mass diffusion on MHD natural convection flow of a visco-elastic fluid in slip flow regime has been studied under the following conditions : (i) suction velocity normal to the plate is constant, (ii) the free-stream velocity oscillates in time about a constant mean, and (iii) convection is produced by simultaneous diffusion of mass and thermal energy. The equations governing the problem have been solved approximately for velocity, temperature and concentration distributions. The flow phenomenon has been characterized by slip parameter, temperature jump coefficient, concentration jump coefficient, Grashof number, modified Grashof number, Schmidt number, and Hartmann number. A comparative study between Newtonian and non-Newtonian, for rarefied and non-rarefied states have been made.

In sixth, chapter an analytical study has been presented which describes the effects of thermal and mass diffusions on magnetohydrodynamic free convection flow of a rarefied gas along a vertical porous plate under the conditions : (i) suction velocity normal to the plate is constant, (ii) the free stream velocity oscillates in time about a constant non-zero mean, (iii) convection is caused by interaction of force of gravity and density differences as a result of combined mechanism of diffusion of energy and chemical species, and (iv) the magnetic field is considered small so that the induced magnetic field is negligible while the viscous dissipation effects are taken into the consideration. The problem which is governed by the coupled non-linear equations is solved approximately for velocity, temperature and concentration fields. The effects of mass diffusion and magnetic field on velocity, temperature, the amplitude and the phase of skin-friction and the rate of heat transfer have been studied graphically. Mean skin-friction and mean rate of heat transfer are entered in tables. During the course of discussion a comparison between rarefied and non-rarefied gas has been made. From chapter second to fifth the discussions for non-Newtonian fluid are confined to a visco-elastic fluid.

Bibliography of the research papers and books concerning the subject matter of the present thesis is given in detail at the end of this thesis alphabetically.

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CERAMIC ENGINEERING

PHYSICO-CHEMICAL INVESTIGATION ON CALCIUM ALUMINATE CEMENT

Mahammad Mujtaba Ali Sup. *Dr. V. K. Singh*

The work embodied in the thesis has been done on monocalcium aluminate which is the main constituent of high alumina cement. The study has been carried out in the following steps :

(1) Formation of calcium aluminates :

1 : 1 mix of $CaCO_3$ and Al_2O_3 was fired at 1200, 1250, 1300 and 1380°c for different reaction time. The partially reacted samples were analysed by x-ray diffraction technique. Unreacted lime in the samples was also estimated. It was observed that formation of C_3A, $C_{12}A_7$, CA_2 and CA_6 phases occur along with CA during reaction. The proportions of different phases vary depending upon reaction temperature and time. The high lime aluminates are formed in higher amount in the beginning of reaction. These intermediate phases get converted to equilibrium phase CA when the reaction is completed.

Differential thermal analysis of 1 : 1 mix has shown an endotherm at 850-950°c which is due to decarbonation reactionproducing fresh CaO. This CaO reacts with Al_2O_3 and forms different aluminates. The exothermic nature has been observed between 1100 to 1300°c which is due to formation of various aluminates. A small endotherm at 1355°c is due to eutectic reaction of C_3A and CA. Formation of $C_{12}A_7$ by this reaction is probable which is shown by sharp exptherm at 1365°c. $C_{12}A_7$ formed melts at about 1390°c and simultaneously other aluminates are formed.

It has been observed that the ultimate phase formed in the aluminate formation depends upon the proportion of oxides. The rate of CA formation from 1 : 1 mix of CaO and Al_2O_3 is faster than the rate of C_3A formation from 3 : 1 mix of CaO and Al_2O_3. The rate of formation of intermediate phases in 3 : 1 mix is much faster than the rate of formation of intermediate phases in 1 : 1 mix of above oxides under similar experimental conditions.

Kinetics of CA formatien has been studied by comparing area of peak of CA at $2\theta = 30.15°$ in diffractograms of partially reacted samples with the area of same peak for standard DA obtained by repeated firing

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of 1 : 1 mix of $CaCO_3$ and Al_2O_3 until the reactants and the intermediate phases have disappeared. The phase boundary controlled reaction equation $1-(1-x)^{1/3}=Kt/r^2$ was used to explain the formation of CA. K values were taken as a measure of rate constant and the activation energy for CA formation was determined from Arrhenius plot. A value of activation energy equal to 38 kcal $mole^{-1}$ was obtained for CA formation. Activation thermodynamic functions were also calculated.

(2) Formation of CA_2 :

1 : 1 mix of CA and Al_2O_3 leading to CA_2 formation was studied at 1350, 1400 and 1450°c using x-ray diffraction technique. The phase boundary controlled reaction equation has been used to determine activation energy for CA_2 formation. The value of activation energy obtained is 34 kcal $mole^{-1}$.

(3) Sintering of CA :

Sintering of CA was carried out using compacts of -45 and -53 +45 micron powders. Samples were fired at 1350, 1400, 1420, 1440 and 1460°c for various reaction time. The -45 micron powder yields about 97 percent of theoretical density in two hours at 1460°c. Log-Log plot of shrinkage vs time was used to study mechanism of sintering. Volume diffusion was found to be the dominant mechanism of sintering. Apparen diffusion coefficient has been calculated by using shrinkage equation,

$$\frac{\Delta L}{L_0}=\left(\frac{20\sqrt{a^3D}}{\sqrt{2}\,kT}\right)^{2/5}r^{-6/5}t^{2/5}$$

Microscopic studies of sintered pellets of CA were carried out using optical and electron microscopes. Appreciable grain growth has been found during densification which affects the rate of shrinkage after initial sintering. Temperature dependence of apparent diffusion coefficient has been used to calculate activation energy which is 167 kcal $mole^{-1}$. Values of apparent diffusion coefficients were found to be lower than interdiffusion between CaO and Al_2O_3.

(4) Properties of CA and its mixes with Al_2O_3 :

CA and its mixes with Al_2O_3 have been studied for thermal expansion, compressive strength and PCE values. Thermal expansion starts from 350°c and limiting values were obtained around 800°c. The compressive strength of hydrated samples of mixes of CA and alumina decreases appreciably when alumina content is increased. In the fired mix strengths were found lower than the strengths obtaincd due to hydraulic bonds. The PCE values of mixes were found to increase with increase in alumina content.

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CHEMICAL ENGINEERING

PHYSICO-CHEMICAL STUDIES ON UTILIZATION OF FELSPAR MINERAL WASTE FOR MAKING IMPROVED BUILDING MATERIALS FROM UNSUITABLE SOILS

Satya Prakash Sup. *Dr. V. C. Joshi*

Section I

Use of Felspar Mineral Waste for Improved Bricks from Unsuitable Soils

Brick is one of the main building material employed for building construction since ages and it will be used for years to come. The demand of brick is increasing day by day as housing problem rises in urban and rural areas due to growth of population and migration of people from one place to other in search of employment. The current Five Year Plan envisages the requirement of brick of the order of 2,500 crores per year which in itself is a collosal task for brick industry.

From brick manufacture point of view the best clay available in the country is alluvial soil of Indo-gangetic plain which offers none of technical difficulty in making bricks. The soils obtained in rest (about two third) of the country are not considered suitable for brick making due to one or other reason. In such areas most of the constructions are made over R. C. C. frame structure and poor quality bricks made of inferior soil are used only for partition walls. These bricks are not found suitable for construction of load bearing walls.

The major groups of unsuitable soil in India can be classified as sandy, red murram and block soils. Sandy soil is non-plastic in nature and does not give sufficient strength to the brick after firing. Red murram and black soils are highly plastic in nature which develop severe cracking during drying and firing. Out of these soils brick cannot be made as such.

Felspar mineral waste is found in some of these areas which can be utilised for making improved bricks from unsuitable soils. This thesis is an attempt to obtain good quality bricks from such inferior soils by mixing them with felspar mineral waste. Investigations have been carried out for the study of physico-chemical characteristics of felspar mineral waste and three samples of inferior soil. Their particle size distribution chemical analysis, surface area, plastic properties and mineralogical composition have been studied. X-ray, D. T. A., T. G. A. and petrographic method of analyses have been employed.

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Effect of additions of felspar mineral waste in three soil samples has been studied as to how their plasticity, moulding, drying and firing characteristics vary. The ultimate improvement in final products have also been studied by testing the desired properties of finished products. X-ray diffraction method has been employed for the study of qualitative changes taking place after firing in the samples with and without addition of felspar mineral waste.

It has been found that addition of 20% felspar fines in sandy soil has improved the workability of soil and increased the strength of briquettes after firing.

Addition of 40% felspar fines in black soil which is highly plastic in nature and poses problems in all the three stages of moulding, drying and firing, has improved the workability of soil and checked cracking of briquettes during drying and firing. It was not possible to get briquettes made out of black soil as such because it cracked into pieces within few hours of drying. During firing stage also it develops severe cracking. This cracking is due to heavy shrinkage during drying and firing stage. Addition of 40% felspar fines in black soil have reduced the heavy shrinkage and thus checked the cracking during drying and firing.

Addition of 20% felspar in red murram soil which also behaves like black soil to some extent improve the moulding, drying and firing characteristics in similar way as in case of black soil.

The physico-chemical studies of all the three samples of inferior soil and felspar fines have been studied in detail by X-ray diffraction, D. T. A., T. G. A., chemical analysis and petrographic analysis. The properties of final products have also been tested for their suitability in ultimate use. The phase development after firing of samples with and without felspar fines has also been studied with the help of X-ray diffraction.

Section II

Use of Felspar Mineral Waste in Development of Low Temperature Glazes and Ceramic Colours for Red Burnt Clay Tiles

Another important use of felspar fines has been found in development of low temperature maturing glazes and ceramic colours for red burnt clay tiles. These compositions are free from lead oxide, hence they have no toxic effect for their use in potteries. As they have maturing temperature range below 1000°C they can be used for colouring red burnt clay tiles.

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The compositions have been developed using felspar mineral waste as one of the constituent alongwith other cheap raw materials. Hence the cost of these compositions is within economic limit. Five glaze colours suited for natural red, blue, green, yellow and black have been developed. The molecular formulae have been calculated and method of their application has been described.

The properties of developed glaze compositions alongwith their structure have been studied and tested with the help of X-ray diffraction. It was found that all the raw materials used for making batches have melted in a uniform glass without any crystallisation or devitrification at maturing temperature.

In conclusion it is found that felspar mineral waste can be utilised in bulk quantity for making improved bricks from unsuitable soil. Another important use of felspar fines has been recommended for development of low temperature maturing glazes and ceramic colours for red burnt clay tiles.

TO STUDY THE MANUFACTURE OF VEGETABLE OIL (RICE BRAN OIL) BY SOLVENT EXTRACTION PROCESS

Abhay Sah Sup. *Dr. B. K. D. Agrawal*

In India, next to the import of petroleum crude we have been paying heavily in foreign exchange for import of over 10 lakh tonnes of edible oil each year at an average cost of over Rs. 800 crores. What is more distressing is that against the recommended per capita consumption of 20 kg of edible oil per year the average per capita consumption in our country is hardly 4.5 kg. Even at this low consumption we are short by more than a million tonnes which is expected to be two million tonnes by 1985.

Whereas India has potential to produce 6 to 7 lakh tonnes of rice bran oil but against this we have produced 1.5 lakh tonnes of rice bran oil in 1981-82 starting from 500 tonnes in 1960, Still it is all the more necessary to produce more of rice bran oil and as import substitute. At present the rice bran oil is used for industrial purposes such as soap making and last year 5000 tonnes have been utilized for hydrogenating it for making vanaspati.

Rice milling industry is one of the largest agro-based industry in the country. There are reported to be 91,154 rice milling units spread throughout the country. Next to China, India is the second largest producer of rice in the world. We here produced 65.3 million tonnes of rice in 1979-80.

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Hence on the basis of 6% bran content on an average we have a potential of 40 lakh tonnes of rice bran which contain on an average 15 to 25% of oil.

Rice bran is the brown layer existing between the rice and the outer husk of the paddy. The bran is obtained as a bye-product in rice milling during polishing of rice. One of the features of rice milling industry in India is that it consists of large number of units having obsolete technology for example huller type. These units not only result in low out turn of rice but also produce bran which have lower oil content. Rice bran obtained in these hullers are mixture of husk and broken rice.

However, in the rubber roller sheller type rice milis bran is obtained separately and this has a higher oil content. The oil content of the rice bran is also affected by the pre-milling treatment of paddy. It is known that the bran obtained from the parboiled paddy contains higher percentage of oil than a bran obtained from raw paddy.

It has been reported that the increase of FFA in rice bran during storage takes place due to the hydrolysis of triglycerides by an enzyme known as lipase. There is definite evidence that the enzyme lipase is present mostly in the layer just peripheral to the aleurone layers while the oil is found to be localised in the aleurone layers of the rice. The enzyme and the oil layer are compartmentalized and do not come together in the resting grain.

However as soon as the bran surface is injured as it happens during milling the enzyme is brought together with the oil layer and the lipase enzyme is triggered into activity. This goes on increasing the free fatty acid content of the oil in bran.

A characteristic feature of rice bran oil is the presence of 1-5% on an average. This wax is very much similar to carnuba wax in properties and has a high melting point of 72.84°C. The following are the components of Rice Bran oil.

Important components of Rice Bran Oil

S. No.	Name	Percentage	Remarks
1.	Toeopheral	2-3%	Which is Vitamine (E) and works as an anti-oxidant in oil.
2.	Squalene	2-2.5%	It is of considerable pharmaceutical interest
3.	Oryzanol	1-2%	It is a ferulic ester of triterpene-alcohol accelerates human growth, useful to autonomic nerve, helps harmonal secera-tion and lowers cholestrol serum level

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Visualising the vast potential and importance of rice bran oil in our economy this study was undertaken.

As petroleum based solvents may be in short supply in future, hence keeping this in view ethyl alcohol which is an agro based solvent was tried as solvent to extract rice bran oil. It was found experimentally that alcohol can as also serve as a solvent but the time to reach 1% residual oil content in case of alcohol is higher than in case of Hexane. It was also seen that the cancentration of ethyl alcohol and the moisture content of the rice bran pellets also affects the rate of extraction,

Refining rice bran oil poses great problem due to the presence of wax and other impurities. Hence refining of crude rice bran oil was done by various methods so that the refining factor could be kept as minimum as possible. For this solvent refining was done using pyridine and ethyl alcohol as selective solvents.

Apart from using solvents for refining, several additives were used prior to alkali refining so that the refining loss could be reduced considerably.

Dewaxing of rice bran oil was also experimentally done. It was found that the separation of wax from the oil is attributed to the emulsification of wax and hydration which is accomplished in presence of aqueous solution of solubilizers.

This partial removal of wax and free fatty acids considerably helps reducing the refining losses. The refined oil by these methods was much clearer than the crude oil directly refined.

The use of additives and solubilizers greatly helped in reducing the refining losses.

Particle size is one of the most important variable iufluencing the rate of extraction of crude lipids from oil bearing material with solvents. Rice bran is a floury material and any attempt to extract the oil directly from the flourly material poses problem due to the production of fines. It prevents percolation of the solvent and also channelises the flow of the solvent through the bran. Hence rice bran needs granulation or pelletization. However the minimum pellet size considered in design or operation is limited by the production of fines.

It was experimentally found that the rice bran and rice bran pellets—Hexane system, the size of the pellets should be such that the surface area/gm is maximum. An equation has been also proposed which correlates that the time to 1% residual oil is an exponential function of the surface area per gram of the pellets. It was found that time to 1% varies inversely to 2.89th power of the surface area/gm of the pellets.

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STUDIES ON SCRAPED SURFACE HEAT EXCHANGER

Kaushal Kumar Srivastava Sup. *Dr. Uma Shankar*

Scraped surface heat exchangers (SSHE) are widely used in many process industries including processing of highly viscous liquids. These heat exchangers are either of thin film type or Votator (liquid full) type.

Sufficient published information is available on heat transfer in SSHE but other aspects like power consumption, flow behaviour etc, have not been studied in much detail. No information is available for pressure drop in SSHE. Realising this deficienco in the available published information-Indo-U. S. Binational Workshop in Heat Transfer Engineering held in 1982 emphasized the need of studying SSHE in greater details.

In the present investigation pressure drop, power consumption and heat transfer measurements have been made simultaneously in a full size spring loaded SSHE using glycerine-water mixtures of different composirions as test fluids. Effects of operating parameters such as mass flow rate speed of rotation, shaft diameter, number of rows of blades and viscosity of the fluid are investigated. Results are interpreted in terms of a boundary layer model proposed specificall for the SSHE. Empirical, semiempirical and theoretical equations for pressure drop, power consumption and heat transfer are alsn proposed.

Result and Discussion

Three possible modes of flow are suggested in a SSHE with avial flow and rotating shaft.

(i) laminar flow without vortices when speed of rotation is very low,

(ii) laminar flow with vortices, when rotational speed is increased at small flow rates, and

(iii) turbulent flow without vartices, when both axial flow and rotational flow velocities are large.

Probable velocity profile for SSHE without axial flow and narrow clearance between blade tip and wall is obtained theoretically as :

$$u_x = -\frac{3\pi\alpha\eta^2_b d_s N}{(d_t - d_s)^2} y^2 + \frac{\pi d_s (1 + 3\alpha\eta^2_b) N}{(d_t - d_s)} y \qquad (1)$$

From this velocity profile, drag coefficient is estimated as

$$(\phi_2) = \frac{4}{\pi} \frac{d_s}{d_t - d_s} (1 + 3\alpha\eta^2_b) \, Re_r^{-1} \qquad (2)$$

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terms α and η_b in above equation are functions of number of blades and magnitude of clearance respectively. For fixed clearance, drag coefficient varies inversely with rotational speed and power consumption is proportional to N^2, which means that SSHE behaves like anchor agitator. But in spring loaded SSHE, clearance is created as a result of lubrication effect and is a function of rotational speed and viscosity of liquid. Accurate estimation of this clearance is very difficult. Therefore unlike other close-clearance agitators no direct relationship exists between power number or drag coefficient and rotational Reynolds number.

Existence of axial flow makes the flow situation in SSHE more complex. Empirical correlations for pressure drop are obtained as :

$$\frac{\triangle P_r}{\triangle P_o} = (Re_r/Re_a)^{0.167} \quad \text{for } Re_r/Re_a < 4 \tag{3a}$$

and

$$\frac{\triangle P_r}{\triangle P_o} = 0.087\,(d_s/d_t)^{-1.4}\, n^{0.66}\, (Re_r/Re_a)^{0.8} \text{ for } Re_r/Re_a > 4 \tag{3b}$$

These empirical results are used to derive expressions for drag coefficient and finally the expression for power consumption is obtained as :

$$N_p = 56.96\, K(d_t/d_e)^2\, (d_s/d_t)^{-1.4}\, n^{0.66}\, Re_a^{0.2} Re_r^{-1.2} \tag{4}$$

Experimental data are used to determine the valua of K as equal to 3.51. Greater influence of rotational speed or time interval between two successive scraping suggests that most of the power is consumed either in scraping against the wall and/or in dissipation near the wall.

As a result of rotation of blades the entire cross section of heat transfer tube is swept with high velocity. Due to clearance, liquid near the wall remains stationary. This leads to the hypothesis of formation of boundary layer at the wall in a segment equal to separation between two adjacent blades. Heat transfer from wall to bulk takes place through this layer. Heat transfer coefficient in the boundary layer has been proposed in the following dimensionless form :

$$Nu = 1.299\, Re_r^{1/2}\, Pr^{1/3}\, n^{1/2} \tag{5}$$

Above correlation is found in good agreement with experimentally observed values of scraped side heat transfer coefficient. It is also observed that experimental results of earlier researchers can be correlated fairly well with the proposed equation,

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Frictional heat due to rotation of scrapers are substantial fraction of total heat transfer in SSHE. When SSHE is used to cool the material this undesirable fraction of heat becomes important. Foregoing analysis and results show that frictional heat is proportiocal to $N^{1.8}$ and $n^{0.6}$ whereas total heat transfer is proportional to $N^{0.5}$ and $n^{0.5}$. Therefore there must be some limit to rotational speed for maximum net heat removal. Expressions are suggested for optimum rotational speed. However, it is advisable to consider power number and Re_r/Re_a as design and scale up parameters for SSHE. Further emphasis should be to increase the number of blades instead of speed of rotation to get the desired number of scrapings in a given time.

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ELECTRICAL ENGINEERING

TRANSIENT FIELD OVERVOLTAGES IN RECTIFIER EXCITED SYNCHRONOUS MACHINES DURING SEQUENTIAL 3—PHASE FAULT

Rabindra Nath Bandopadhyaya

Sup. *Dr. V. S. Subbarao*
Co-Sup. *Dr. G. S. Raju*

In a synchronous machine with rectifier excitation system, large reverse voltage may be induced across the field when following a disturbance, the field current tends to flow in the negative direction and is blocked by the rectifier. Earlier investigations showed that out of the various types of possible transients, a line to line fault was perhaps the severest as far as the reverse field overvoltages are concerned. The present work extends the above investigations to cover the field transients under the condition of a sequential 3—phase fault, in which a line to line fault develops into a 3—phase fault after a small time delay.

Recent studies have indicated that for accurate analysis of the synchronous machine field transients, the conventional mathematical model has to be modified by including the effect of mutual leakage fluxes linking two of the three direct axis windings, viz. armature, field and damper. A further possible extension to the modification of the model has been examined and an improved equivalent circuit has been proposed Detailed computer simulation of the more accurate machine model has been done and numerical solutions of the differential equations under the conditions of line and sequential 3—ph. faults have been obtained. These are subsequently used for comparison with the approximate analytical results for specific cases.

A simplified mathematical procedure with suitable approximations resulting in a closed form solution of the field transients under line to line and sequential 3—ph. faults has been obtained. The conditions under which the field current may become negative and hence be subsequently blocked by the rectifier have been found for these faults. Analytical expressions for the reverse field voltages due to the blocking of the negative field current have been derived for machines both without and with prefault load. To fecilitate the analysis, all resistances are initially neglected and subsequently approximate correction for resistances is made. The results of the analytical solution compare well with the more accurate numerical results establishing the validity of the analysis.

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Although a detailed study of the eddy current effect in the rotor body is considered outside the scope of this work, the results as obtained above have been modified by considering an equivalent eddy current resistance in the computer simulation as suggested in the literature. The results indicate that whereas the possibility of reverse field voltage being induced under the normal 3—ph. fault (simultaneous shorting of phases) is usuallyrare, the field voltages during sequential 3-ph. fault are generally much greater than those under line to line fault.

The worst case appears to be the consequence of development of such a sequential fault on a salient pole machine with laminated rotor operating initially with a heavy leading load, in which case the overvoltage may be really severe.

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METALLURGICAL ENGINEERING

SYNTHESIS AND CHARACTERIZATION OF SOME BINARY AND TERNARY TRANSITION METAL-METALLOID ALLOY SYSTEMS

Mrityunjaya Singh

Sup. *Dr. S. Bhan*
Co-Sup. *Dr. V. N. Singh*

Technological advancement, which is an indispensable component of the evolution of modern civilization, rests essentially on the knowledge of synthesis, characterization and application of materials. The process of alloying occupies a special significance in the science of materials. Formation of solid solutions, intermetallic and electron phases through alloying leads to the synthesis of metallic materials. The ultimate goal of which is to correlate structure and properties and fabricate materials according to desired specifications. The structure of these phases depends on the composition of the alloy and temperature, provided the alloy is in equilibrium. Phase diagrams or equilibrium diagrams make it possible to classify alloys into groups, according to their structures and to study them with regard to their general properties. A thorough knowledge of the construction, significance and interpretation of the phase diagram is the major pre-requisite for understanding the structure of alloys and their properties.

Transition metal-metalloid intermetallics represent the widest range of alloy formation. These intermetallics are known to be of great technological importance due to their special semiconducting, superconducting and magnetic properties. Some of these intermetallics undergo structural transformations by application of pressure and high cooling rates. Apart from their key role in advancement of modern industries, there is a profound interest in the elucidation of principles underlying the alloying behaviour of these intermetallics. Motivated by their special significance, as indicated in the foregoing, the present investigation was carried out. The central theme being "Synthesis and Characterization of Some Binary and Ternary Transition Metal-Metalloid Alloy Systems."

The thesis comprises of seven chapters. First Chapter viz., Structure and Theories of Alloy Phases, discusses briefly the historical development and present state of affairs with regard to various alloy theories. Some important topics described briefly are : structure of alloys, factors influencing crystal structure of alloys and electron theory of alloy phases. This chapter also highlights the formation of long period superlattice structure of alloys and structure of non-metallic compounds.

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The second Chapter deals with some important features of vapour deposition, rapid solidification, X-ray diffraction, Transmission and Scanning electron microscopic techniques, used in the present investigation. Chapters Three to Seven deal in detail with the experimental investigations on the constitution and structure of Cu – Ni - Te, Cu – Ni - Se, Ag – Ni – Te, V_3Si – Fe_3Si and Fe – Sn systems.

The third Chapter concerns with the structure of different binary phases, ternary isotherm of copper-nickel-tellurium system at 743 K and electron microscopic study of some melt quenched alloys. Occurrence of two new ternary phases has been established. A new face-centred cubic phase with lattice parameter a = 1.155 nm, related to Cu_5FeS_4 type, is found in $Cu_{20}Ni_{42}Te_{38}$ alloy. This phase is found to be homogeneous at the composition $Cu_{13\cdot5}Ni_{47}Te_{38\cdot5}$. The alloy $Cu_{20}Ni_{42}Te_{38}$, on quenching from 823 K, has a typical basket-weave type of microstructure. Another new hexagonal phase, related to NiAs(B8) type, with a = 0.395 nm and c = 1.072 nm is found in $Cu_{55}Ni_5Te_{40}$ alloy. The composition upto which this phase is homogeneous is $Cu_{52}Ni_8Te_{40}$.

The $NiTe_{1+\times}$ phase, with defective NiAs type of structure has a large homogeneity range between $NiTe_{1\cdot08}$ and $NiTe_{2\cdot00}$. This phase is found to have a large homogeneity range in the ternary isotherm, with no ordering of vacancies in the entire composition range. Copper atoms goes to the unfilled octahedral and tetrahedral voids present in this structure.

In order to study the effect of high cooling rates on structure, some alloys were melt quenched using 'gun' technique. Solid solubility of nickel in Cu_2Te phase has been increased upto ~11 at.% nickel by melt quenching in comparison to 2 at.% at 743 K, Structural characterization of as quenched and annealed foils has been carried out using Transmission electron microscopy and X-ray diffraction.

The phase relations in the Cu – Ni – Se system at 703 and 573 K have been presented in fourth Chapter. At 703 K, a large liqnid phase field in the Cu-Se system dominates the selenium rich portion of the isotherm. In the Ni-Se system, three phases viz., Ni_3Se_2, $NiSe_{1+\times}$ and $NiSe_2$ are found stable at this temperature. The Ni_3Se_2 phase has homogeneity range towards lower valence electron concentrations in the ternary isotherm. Its homogeneity extends upto 8 at.% copper. The NiSe phase shows large homogeneity in the binary system but it does not extend in the ternary system. On the Cu-Se line, two phases viz., Cu_2Se and $Cu_{2-\times}Se$ were observed at 703 K. Homogeneity ranges of monoclinic Cu_2Se and f.c.c. $Cu_{2-\times}Se$ phase extend to ~2 at.% nickel in ternary iso-

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therm. Rapid quenching of the alloys of Cu_2Se - Ni_3Se_2 line, results the same structure as 703 K with slightly different lattice parameters. This increase in lattice parameters is due to larger concentration of vacancies in splat foils.

At 573 K, some other phases are stable in the selenium rich portion of the isotherm. These are hexagonal CuSe with a = 0.395 nm, c = 1.731 nm and orthorhombic $CuSe_2$ with a = 0.5026 nm, b = 0.6193 nm and c = 0.735 nm. Hexagonal NiSe phase dissolves ~5 at.% copper but no homogeneity of nickel in CuSe phase has been found. Alloys lying on the $CuSe_2$ – $NiSe_2$ line have simple two phase structure.

The fifth Chapter deals with the ternary isotherm of Ag – Ni – Te system at 873 K and structural characterization of bulk and thin film phases of nickel tellurides, with emphasis on the transformation behaviour. In the ternary isotherm at 873 K, only monoclinic Ag_2Te phase with a = 0.815 nm, b = 0.449 nm, c = 0.811 nm and $\beta = 112°60'$ is stable on the Ag – Te line. Existence of two phases viz., tetragonal Ni_3Te_2 and hexagonal $NiTe_{1+x}$ with wide range of homogeneity in the ternary isotherm, has been established. Solid solubility of nickel in Ag_2Te is found to be ~5 at.%. Tetragonal Ni_3Te_2 phase dissolves 5 at.% silver at this temperature. Lattice parameters of $Ag_5Ni_{55}Te_{40}$ is a = 0.378 nm and c = 0.607 nm. Alloys of the Ag_2Te – Ni_3Te_2 line shows simple two phase structure.

The as-grown thin films of $NiTe_2$ alloy were found to correspond to bulk phase with a = 0.39 nm and c = 0.53 nm. On pulse annealing, these films underwent a transformation with cubic structure, a = 0.74 nm. Further pulse annealing, resulted the growth of large single crystal regions. The transformed regions consisted of single crystals, with planar faults and twins. Analysis of diffraction patterns from these crystals revealed the presence of modulated phases which were akin to polytypes. The modulated phase is 2H or 6R. Further annealing results the highly disordered structure.

Chapter six deals with the synthesis and characterization of V_3Si – Fe_3Si system. Existence of a new phase at 673 K, around $V_{25}Fe_{50}Si_{25}$ composition has been established. This phase has orthorhombic structure with a = 0.7517 nm, b = 0.7214 nm and c = 0.6917 nm and unstable at higher temperatures. Solid solubility of V in Fe_3Si is 25 at.% at 1273 K. Substitutional alloying of transition metals in Fe Si largely depends upon the electronegativity of the substitutional elements. Atoms more electronegative than Fe goes into Fe A while less electronegative as V, Cr and Mn goes into Fe B sites.

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Chapter Seven deals with Fe-rich side of the Fe-Sn phase diagram. The present work on this system led to few important revelations. The alloy $Fe_{75}Sn_{25}$, which should be single phase at 1073 K, contains α - Fe and a transformed phase on quenching from this temperature. It confirms that Fe_3Sn phase could not be retained on quenching. High temperature X-ray diffraction study of $Fe_{75}Sn_{25}$ alloy indicates the presence of a new f.c.c. phase with a = 0.4394 nm at 1373 K. In $Fe_{70}Sn_{30}$ alloy, existence of two new orthorhombic phases have been established. Orthorhombic phase (II) has been observed in the temperature range 973 to 1073 K, with lattice parameters a = 0.7289 nm, b = 0.9853 nm and c = 0.7162 nm at 973 K. Orthor-hombic phase (I) exists in the temperature range 1223 to 1373 K along with A2. Lattice parameters of this phase at 1373 K are found to be a = 0.5689 nm b = 0.5625 nm and c = 0.5560 nm. High temperature X-ray data has been used to modify the Fe – rich side of the phase diagram and revised tentative phase diagram is presented.

Electronic structure and stereochemistry of copper and silver-rich chalcogenides has been highlighted in Appendix. Electronic structure of these chalcogenides has been discussed in terms of orbital interactions of cation and anion. Electrical conductivity, magnetism and homogeneity ranges of these chalcogenides have been explained on the basis of holes in valence band. Stereochemistry of Cu^+ and Ag^+ in these compounds has been discussed in terms of bonding and hybridization.

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PHARMACEUTICS

CHEMICAL INVESTIGATION OF SOME NATURAL DRUG PRODUCTS

Ashutosh Sup. *Dr. S. Ghoshal*

The plant kingdom has been the benefactor of mankind since the ancient times. People everywhere have attempted to utilize the flora of their respective regions for the relief of their ailments. Most of our present day knowledge of therapeutic agents has developed from the study of the herbal and folk medicines. In view of this, it was thought worthwhile to take up a systematic chemical investigation of some natural drugs which are used either in traditional system of medicine or in popular medicine.

The study was primarily directed to the Secondary metabolites of the selected natural drugs. Among the secondary metabolites, alkaloids, polyphenolics and triterpenoids occupy significant position in regard to chemistry and biological significance of natural drugs. Hence these three types of constituents have been studied in detail. Thus, the thesis constitutes isolation and structure determination of alkaloids of *Haemanthus kalbreyeri* Baker and *Zephyranthes flava* Roem & Schult (Family, Amaryllidaceae); 6-aryl-2-pyrones of *Gentiana pedicellata* Wall (Family, Gentianaceae); and tetracyclic triterpenes of *Geastrum asper* Lloyd (Family, Geastraceae).

While *H. kalbreyeri* of European origin was investigated before and reported (Wildman, 1960) to contain several alkaloids comprising of crinane-, powellane-, haemanthaminetype ring systems, the species naturalized in India has not been chemically examined before. The variation in the alkaloidal patterns of taxa with ecological variation is a well documented phenomenon. It was, therefore, thought worthwhile to record the variations, if any, in the alkaloidal patterns of *H. kalbreyeri* of Indian origon vis-a-vis those produced by the species in Europe.

Z. flava has not been chemically examined before. The genus *Zephyranthes* is a well know producer of a variety of alkaloidal skeleta encountered in the family Amaryllidaceae. From this point of view, the exploration of this species was deemed to be worthwhile.

Gentiana pedicellata Wall was explored before, elsewhere partially. The chemical constituents reported were only known flavanoids. The

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experience of the present investigator was quite different. Initially, however, he was inclined to chemically examine this species in view of the reputation of the genus in producing a variety of polyoxygenated xanthones (Ghosal *et al.*, 1975). The expectation was not belied since a new type of rarely occurring polyphenolics, viz. the 6-aryl-2-pyrones were encountered for the first time in this family.

The species *Geastrum asper* Lloyd was not chemically investigated before. Two new tetracyclic triterpenic acids were obtained from this species which were found to exhibit significant antifungal activity.

From the roots and bulbs of *H. kalbreyeri*, collected at the flowering time, two new alkaloids, viz. kalbretorine (I) and kalbreclasine (II) were isolated and characterized on the basis of chemical transformation and comprehensive spectral analyses. Additionally, hippadine (III) and pratorinine (IV), the alkaloids previously encountered in the genus *Crinum* (Ghosal et al., 1981), and Lycorine-1-*O*-B-D-glucoside (V), a glucoalkaloid reported before in the genus *Pancratium* (Ghosal *et al.*, 1983), were also isolated and characterized. Along with these, four well known alkaloids, viz. lycorine (VI), haemanthamine (VII), haemanthidine (VIII) and narciclasine (IX) were also isolated and identified. While lycorine, haemanthamine and haemanthidine were previously encountered in *H. kalbreyeri* of European origin, this is for the first time that hippadine, pratorinine, lycorine-1-*O*-B-D-glucoside and narciclasine have been reported in this species (of Indian origin).

From the roots and bulbs of *Z. flava* Roem & Schult, a new glycoalkaloid, which we named, narciclasine-*O*-xyloglucoside (X) and six known alkaloids. viz. lycorine (VI), haemanthamine (VII), haemanthidide (VIII), narciclasine (IX), crinamine (XI) and maritidine (XII), were isolated and characterized. Likewise, the extractives of the seeds afforded lycorine, haemanthamine, haemanthidine and maritidine, whereas extract of flowers and flowering stems yielded lycorine-*O*-glucoside (V) as the major constituent in addition to the commonly encountered alkaloids of this species. Some interesting spectral features, as revealed during the spectral analyses (^{1}H NMR in different solvents, CD) of crinamine and maritidine are reported for the first time.

Three new 6.aryl-2-pyrones, viz. pedicellin (XIII), pedicellanin (XIV) and pedicellatin (XV), in addition to four known compounds, viz.gentianine(XVI), loliolide (XVII), erythrocentaurin (XVIII) and ursolic acid (XIX), were isolated and characterized from the whole plant of *Gentiana pedicellata* Wall. The compounds (XVI) to (XIX) are the typical chemical

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characters of the genus *Gentiana* (Ghosal *et al.*, 1983a). Further investigation of the species has now resulted in the isolation and structure determination of two more new 6-aryl-2pyrones, which we named pedicelloside (XX) and pediursolate (XXI).

Two new C_{21}-carboxylated tetracyclic triterpenic acids, viz. asperolic acid (XXII) and dehydroasperolic acid (XXIII), were isolated from the spores and outer coverings of *Geastrum asper* Lloyd. The characterization was accomplished by chemical correlation and comprehensive spectral analyses.

The activity of narciclasine-*O*-xyloglucoside (X) was studied on the producer (*Z. flava*) and a non-producer plant species (*Pisum sativum*, Family Leguminosae). The compound inhibited the root- and stem-growth in the nonproducer plant at all stages of growth, whereas in the producer plant, the compound initially inhibited but later promoted the root- and stem-growth.

The antifungal activity of asperolic acid (XXII) and dehydroasperolic acid (XXIII), obtained from *Geastrum asper* was studien against three fusaria and one *Aspergillus* species which are known to cause post-wound infection in man and cattle alike in the western region of the Himalayas (foot hills).

STUDIES ON SECONDARY METABOLITES OF SOME MEDICINAL PLANTS

Kulwant Singh Saini Sup. *Dr. S. Ghoshal*

The thesis entitled, "Studies on Secondary Metabolites of Some Medicinal Plants," deals with the isolation and determination, by spectroscopic analyses and chemical correlation, of the structures of alkaloids and polyphenolics of some Indian medicinal plants and screening of physiological activity of the chemical constituents, where possible. The thesis is broadly divided into two parts.

PART—I constitutes the chemical investigation of three alkaloid-bearing previously partially explored amaryllidaceous plants, viz *Crinum latifolium* Linn, *Crinum asiaticum* Linn and *Crinum augustum* Roxb. The present work complements the previous investigations in respect of the

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alkaloidal constituents of these three species. Additionally, the physiological significance of a fully aromatic phenanthridone alkaloid, hippadine, has been evaluated.

In *PART—II*, the chemistry of oxygen-containing polycyclic compounds of a previously unexplored *Canscora* species, viz. *C. diffusa* (VAHL) R. Br. (Gentianaceae), has been described. Additionally, a route for the entry into 7-*des* methylxanthones has been reported.

The objective of isolation of the chemical constituents, was accomplished by splvent-gradient fractionation of the plant extracts followed by extensive column and layer chromatography of the different fractions, as also fractional crystallization of mixture components and derivatization. The structures of the pure compounds were established on the basis of physical properties. comprehensive spectral analyses (UV, IR, MS, ^{1}H-and ^{13}C NMR, $[\alpha]_D$) and. finally, by total or partial synthesis of the molecules and/or their derivatives, where possible.

The organization of the thesis is as follows :

PART—I is further sub-divided into three chapters. In *CHAPTER-I* the current status of research on the naturally occurring alkaloids of the genus *Crinum* (Amaryllidaceae), – their plant sources physical and spectral properties have been reviewed (Sections A—C).

Section—A deals with an introduction to Amaryllidaceae alkaloids, their general features and isolation.

In *Section—B*, the distribution of the alkaloids in the genus *Crinum*, their physical properties (molecular formula, melting points and $[\alpha]_D$) and literature references are given.

Section—C describes the application of modern spectral tools, viz. UV, IR, MS and ^{1}H-and ^{13}C NMR spectra, in the structure elucidation and in exploring some of stereochemical points of the different ring system present in the alkaloids of the genus *Crinum*.

The line drawings of the structures are provided.

CHAPTER—II describes the chemistry of the alkaloids of the three mentioned species, viz. *C. latifolum* Linn, *C. asiaticum* Linn and *C, augustum* Roxb. Six ring systems, viz. phenanthridone, pyrrolophenanthridone and-phenanthridine, 5, 10b-ethanophenanthridine, [2]benzopyrano [3, 4c] indole, *N*-benzyl-*β*-phenethylamine were encountered. The details are distributed in four sections (A–D). The essential features are outlined below.

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Phytochemical investigations of different plant belonging to the family Amaryllidaceae was initiated in this laboratory some five years ago. The present worker joined this stream in 1979 to carry out research in part fulfilment of the requirement for his M. Pharm. degree. After the M. Pharm. degree was obtained (1980), he continued to carry out intensive research in the mentioned areas. The main thrust was given on the isolation and characterization of new alkaloids. The objectives was realized as revealed from the isolation and characterization of eight new alkaloids besides ten known ones.

From the bulbs of the *Crinum latifolium* Linn, which was previously reported to contain only lycorine (XII) (Rangaswami and Suryanarayana, 1955; Rangaswami, 1966), the present investigator isolated and characterized six new alkaloids, two of which belonging to the fully aromatic group, viz. *pratorimine* (I) and *pratosine* (II) others are *1, 2-β-epoxyambelline* (III), *lycorine---* and *β-methocations* (V, VI) and *indolo-7-piperonylic acid* (VII); while the sap-fluid of the flower-stem afforded a new advanced intermediate, viz. *14, 14a-di-O-methyl norbelladine* (IV), Additionally, nine known alkaloids, viz. hippadine (VIII), pratorinine (IX), ambelline (X), tazettine (XI), lycorine (XII), 1, 2-diacetyllycorine (XIII), anhydrolycorin-7-one (XIV), hordenine (XVI) and tyramine (XV), which were encountered before in other amaryllieaceous species, were also isolated and charaterized from this species.

The two pyrrolophenanthridone alkaloids, pratorimine (I) and pratosine (II), are new additions to this series (cf. hippadine and pratorinine, Ghosal *et al*, 1981). These two alkaloids were characterized on the basis of comprehensive spectroscopic analyses, and unambiguous synthesis, the latter following a modified procedure as described in the literature (Humber *et al*, 1954; Benington and Morin, 1962).

Some years ago, Samuel (1975) assigned 1, 2-epoxyambelline structure (without the stereochemical implications) to a new alkaloid, cavinine, from *Hippeastrum punecium* on the basis of only mass spectral evidence. No other information such as isolation, physical and other spectral properties are on record. The present investigator now reports the details of isolation, structure and stereochemistry of 1, 2-β-epoxyambelline (III), obtained from *C. latifolium* Linn. However, the name cavinine is adopted for this alkaloid for future reference.

The alkaloid 1, 2-β-epoxyambelline (III) was found to co-occur with ambelline (X) in approximately 1 : 3 proportion, at all stages of vegetation of *C. latifolium*, which is biochemically significant. 14, 14a-di-O-methyl norbelladine (IV), which had a transient existence, was isolated

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from the sap-fluid of the flower-stem of *C. latifolium.* The structure of this advanced intermediate was proved by its spectral analyses and synthesis.

The search for new alkaloids was further extended to two partially explored species, viz. *C. asiaticum* Linn and *C. augustum* Roxb. From the bulbs of *C. asiaticum*, collected at flowering, a new phenanthridone alkaloid, *8, 9-methylenedioxy-6-phenanthridone* (XVII), was isolated. The characterization of this alkaloid was based on spectroscopic (UV, MS) evidence and by correlation with a previously reported synthetic sample (Mondon and Krohn, 1972). Additionally, the bulbs of *C. augustum* and *C. asiaticum*, provided five previously known alkaloids, viz. lycorine (XII), ambelline (X), crinamine (XVIII), hippadine (VIII) and pratorinine (IX), while tazettine (XI) was isolated from *C. asiaticum.* This is the first report of occurrence of a pyrrolophenanthridone alkaloid in *C. augustum*, which was recently reported to contain other types of alkaloids (Ali *et al.* 1983).

The different batches of the three *Crinum* species were examined for their alkaloids. The alkaloidal pattern of the three *Crinum* species, at any particular stage of ontogeny, were found to be quite similar. It has been found that the total alkaloidal production is highest in the early flowering stages and marked fluctuations of the alkaloid contents occur during the subsequent period of vegetation. The concentration of the pyrrolophenanthridone alkaloids was found to be maximum at pre-and post-flowering stages of *C. latifolium* Linn and the flowers and flowering stems were devoid of these alkaloids.

Another noteworthy aspect of this investigation was the trapping of some reactive alkaloidal intermediates and to establish their identity by spectroscopic analysis and chemical correlation. The detection of the advanced intermediates in plants is important from the point of view of plant biochemistry. One such intermediate trapped was the norbelladine equivalent (IV) described above. Likewise, the isolationindolo-7-piperonylic acid (VII) from *C. latifolium* Linn suggests a possible catabolic route of the pyrrolophenanthri done alkaloids *via* this intermediate. Lycorine-α-and β-methocations (V and VI) have been encountered for the first time as naturally.occurring compounds, the observation is again biochemically significant since it is known that [2] benzopyrano [3, 4g] indole analogues are formed *via N*-methylation of the lycorine analogues.

CHAPTER—III constitutes the pharmacological screening of one of the pyrrolophenanthridone alkaloid; hippadine (VIII), obtained from all the three mentioned species. Prompted by the ontogenic variations of this

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alkaloid, during the intense active growth of the producer plants, the effect of hippadine on reproductivity, e. g. testicular activity of rats, was examined. The alkaloid was found to produce reversible inhibition of fertility in male rats. A decrease in the testicular weight and DNA content and an increase in protein concentration indicated a fall in the relative proportion of freshly divided cells. The weight of accessory sex organs revealed continued production of androgens.

The relevant literature references are incorporated at the end of each chapter.

Part II—deals with the chemistry of another class of compounds, viz. polyphenolics, and is divided into two chapters.

Chapter I—describes the chemistry of flavans and xanthones isolated from a previously unexplored species, viz. *Canscora diffusa* (VAHL) R. Br. This chapter is divided into five sections (A-E).

From the whole plant of *C. diffusa* a new glucosyloxy flavan which was named, *diffutin* (XIX), was isolated. The structure of this flavan was fully established on the basis of spectral analyses and chemical transformations. Additionally, the minor phenolic constituents of this species—nine known free polyoxygenated xanthones, viz. 1-hydroxy-3, 5 dimethoxy—(XX), 1-hydroxy-3, 5, 6-trimethoxy—(XXI), 1, 5-dihydroxy-3-methoxy—(XXII), 1,6-dihydroxy-3,5-dimethoxy—(XXIII), 1,3,6-trihydroxy-5-methoxy-(XXIV), 1-hydroxy-3,5,6,7-tetramethoxy—(XXV), 1,3,5-trihydroxy-6-methoxy—(XXVI), 1,6,7-trihydroxy 3,5-dimethoxy—(XXVII), 1,3,5-trihydroxy -6,7-dimethoxyxanthone (XXVIII), and two xanthone *C*-glycosides, viz. mangiferin (XXIX) and homomangiferin (XXX), were isolated and characterized. The minor xanthonic constituents were previously encountered in a sister species, *C decussata* Schult (Ghosal *et al*, 1977); however, this is the *first* report of the occurrence of the xanthones in *C. diffusa*.

A possible chemotaxonomic significance is envisaged, on the basis of co-occurrence of the polpoxygenated xanthones having similar oxygenation patterns (1, 3, 5-tri-, 1, 3, 5, 6-tetra-, 1, 3, 5, 6, 7-penta-oxygenated) in *C. diffusa* (VAHL) R. Br. as also in sister species, *C. decussata* Schult, together with the absence of flavans in the latter species, which are vicariously represented by mangiferin (XXIX).

Chapter—II deals with the synthetic aspects of the polyoxygenated xanthones. The existing methods of synthesis of polyoxygenated xanthones and their selective methylation and demethylation to synthesize the corresponding hydroxy/methoxy xanthones have been discussed. This revealed that the existing methods were not satisfactory in terms of

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regioselectivity and/or yield for the synthesis of 7-*des* methylxanthones. The present investigator took up the problem at this stage and developed new method for introduction of hydroxy group at 7-position. Thus, 1, 3, 6-trimethoxy-7-hydroxyxanthone (XXXI) was synthesized by opening up of the methylenedioxy ring, according to a published procedure for opening up of this ring in *p*-Ar. CHO/-NO_2 substituted compounds (Kobayashi *et al*, 1980). Thus, treatment of 1, 3-dimethoxy-6, 7-methylene-dioxyxanthone with alkoxides in presence of DMSO afforded 1, 3, 6-trimethoxy-7-hydroxyxanthone (XXXI). This new and simple metdod provided an entry into 7-*des* methylxanthones in good yield.

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FACULTY OF INDIAN MEDICINE

BASIC PRINCIPLES

अगद तन्त्र का क्रमिक विकास

प्रभुनाथ उपाध्याय निर्देशक : डा० लक्ष्मीशङ्कर विश्वनाथ गुरु

मेरे शोधप्रबन्ध का विषय ''अगद तन्त्र का क्रमिक विकास'' है। शोध का मात्र यह उद्देश्य है कि प्राचीन संहिताओं, वेद, उपनिषद्, पुराण, स्मृति, धर्मसूत्र, आयुर्वेदीय एवं आयुर्वेदेतर ग्रन्थों में उपलब्ध अगद तन्त्र विषय (विषविज्ञान) से सम्बन्धित साहित्य का अध्ययन कर विद्वानों के समक्ष उपस्थित करना।

उपर्युक्त विषय से सम्बन्धित विषय आयुर्वेदीय ग्रन्थों में यत्र-तत्र बिखरे हुए रूप में उपलब्ध हैं परन्तु आयुर्वेदीय साहित्य में स्वतन्त्र ग्रन्थ के रूप में उपलब्ध हैं। इस परम्परा में अज्ञात नाम के लेखकों की कृतियाँ ''तार्क्ष्य मंत्र'' ''विष तंत्र'' एवं ''अगद राज तंत्र'' आदि के नाम प्राप्त होते हैं। प्राचीन आयुर्वेद संहिताओं में आचार्य सुश्रुत संहिता ही एक ऐसा ग्रन्थ है जिसमें विषों से सम्बन्धित स्वतन्त्र स्थान (कल्प स्थान) पाया जाता है।

वेदों में विष विषयक साहित्य प्रचुर मात्रा में उपलब्ध है।

अथर्ववेद में विष के दो भेद बताएँ हैं। स्थावर एवं जंगम, इस सूक्त में तीन ऋचाएँ हैं, तीनों ऋचाओं में उपर्युक्त दो प्रकार के विषों का अपाकरण विनियुक्त है। सूर्य, अग्नि, पृथ्वी एवं औषधियों से उत्पन्न विष।

द्यावा पृथ्वी और सप्त समुद्र में विष को व्याप्त होना बताया है। इसके अतिरिक्त सर्प के विष के संदर्भ में तक्षक सर्प के विष का वर्णन है। इसी ऋचा में वर्णावती नामक वृक्ष का उल्लेख है जिसके भावित जल से समस्त प्रकार के विष का निवारण बताया गया है। बभ्रु सर्प एवं तरुणक आदि सर्पों के नामतः उल्लेख हैं। इसी ऋचा में ही सर्प के माता-पिता के रूप में अलगी, विलगी को प्रस्तुत किया गया है। मधु का विषनाशक रूप में उल्लेख है। अथर्ववेद में वृश्चिक विष का उल्लेख है। वृश्चिक के सम्बन्ध में उल्लेखनीय तथ्य यह है कि हेमन्त ऋतु में वृश्चिक का डंक नीचे रहने का सङ्केत प्राप्त होता है।

उपर्युक्त वेद में शृङ्ग युक्त कीटों के विष का भी वर्णन प्राप्त होता है। ऋग्वेद में सूर्य को विषयुक्त जीवों के विषता को दूर करने का वर्णन प्राप्त होता है। साथ ही इसी ऋचा में विष के निवारण के लिए ९९वें क्रियाओं तथा २१ मयूरनियाँ एवं ७ नदियों का उल्लेख प्राप्त होता है। वन्दन नामक विष वृक्ष, साथ ही यक्ष्मा विषनाशक, अश्वावती, सोमवती, अर्जयन्ती नामक औषधियों का उल्लेख है।

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यजुर्वेद में स्पष्ट रूप से उल्लेख है कि भोज्य पदार्थों के माध्यम से विष का प्रयोग किया जाता था। पृदाकु नामक एक ऐसे बलवान सर्प का उल्लेख है जिसे आजकल की दृष्टि से अजगर कहा जाता है। यजुर्वेद में ही मशकों को कष्टदायी रूप में वर्णन करते हुए इनको नष्ट करने का निर्देश दिया गया है।

एक ऐसे विषैले धूम्र का उल्लेख प्राप्त होता है जिससे अत्यधिक अश्रुपात होता है। जिसे हम आजकल की दृष्टि से अश्रुगैस की संज्ञा दे सकते हैं।

उपनिषदों के अध्ययन के पश्चात् आज कुछ उपनिषदों को छोड़कर अन्य उपनिषदों में विष-विषयक साहित्य अनुपलब्ध है। शाण्डिल्योपनिषद् में भद्रासन योग द्वारा विष के निवारण का उल्लेख प्राप्त होता है। सम्पूर्ण गरुडोपनिषद् में विष को नष्ट करने का उल्लेख मन्त्र द्वारा किया गया है। साथ ही इन मन्त्रों को सिद्धि के लिए विधि बनाई गई है। ईशावाश्योपनिषद्

धर्मसूत्र ग्रन्थों में मुख्यतः आचार, विचार, शुद्धीकरण एवं प्रायश्चित्त आदि का वर्णन प्राप्त होता है। विष-विषयक साहित्य यत्र-तत्र सूक्ष्म रूप में दृष्टिगत होता है।

बौधायन धर्मसूत्र में अलर्क विष का उल्लेख करते हुए इसके विष के निवारण के लिए स्वर्ण तथा ताम्र में रखे हुए जल से स्नान करने का विधान बनाया गया है। गौतम धर्मसूत्र में विष से मृत्यु, बन्धन से मृत्यु (फाँसी) तथा आत्महत्या का उल्लेख प्राप्त होता है।

स्मृति ग्रन्थों में सामान्यतः धर्म विषयक साहित्य का व्यापक समावेश है। कुछ स्मृतियों में विष द्वारा मृत्यु एवं सर्प आदि के विषों का वर्णन है। कात्यायन स्मृति में सर्प विष एवं कीट विषों का उल्लेख किया गया है। विष्णु स्मृति के राजधर्म वर्णन के अन्तर्गत स्पष्ट रूप से उल्लेख है कि विष को नष्ट करने के लिए विष विनाशक औषधियों का ज्ञान अत्यन्त आवश्यक होता है। अत्रिस्मृति में अलर्क विष के निवारण के लिए हिरण्योदक मिश्रित घृत का सेवन करने का विधान बनाया गया है। याज्ञवल्क्यस्मृति में न्याय, वैद्यक एवं धर्म के अनुसार ९ प्रकार के दिव्य प्रमाणों का उल्लेख किया है। वर्णानुसार न्यायालय में ब्राह्मण को तुला, क्षत्रिय को अग्नि, वैश्य को जल तथा शूद्र को विष दिव्य प्रमाण के रूप में वर्णित है।

पुराणों में अगद तन्त्र विषयक साहित्य प्रचुर मात्रा में प्राप्त होता है।

वायुपुराण में विशल्या नामक ऐसे द्रव्य का उल्लेख है जिसके सम्बन्ध में उक्ति है कि विषपान के उपरान्त विशल्या धारण करना विष शमन के लिए श्रेयस्कर है। अग्निपुराण में राष्ट्र के अधिपति के लिए राज दरबार में विष के ज्ञान-वान का रहना आवश्यक होता था, यह परम्परा आज भी प्रचलित है। निम्ब पत्र भक्षण से सर्प विष दूर होने का उल्लेख है। इसके अतिरिक्त इसी पुराण में लता आदि का वर्गीकरण एवं चिकित्सा का वर्णन प्राप्त होता है। वृश्चिक विष के निवारण के लिए अताप सेवन या शिखिपत्र, अर्क-दुग्ध पलाश बीज के साथ पीस कर प्रयोग करने का विधान बताया गया है। सर्प एवं कीट विष के लिए तंडुलीयक त्रिवृत्त को घृत के साथ सेवन करने का उल्लेख है। इसी पुराण में सर्प के वंशावली का उल्लेख है साथ ही इनके दंश से साध्यासाध्यता एवं चिकित्सा का वर्णन है। स्कन्द पुराण में सोम कल्प योग का वर्णन प्राप्त होता है जिसके सम्बन्ध में उक्ति है कि इसके प्रयोग से सर्प

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विष प्रभावी नहीं होता। वामन पुराण में वृश्चिक विष, कीट विष का उल्लेख है। चिकित्सा की दृष्टि से कूर्म पुराण में अलर्क विष के लिए विशेष विधान का निर्देश दिया। पागल कुत्ते द्वारा दष्ट करने पर ३ दिन दुग्ध पान करने का विधान है परन्तु ऊर्ध्व भाग में दंशित होने पर द्विगुण तथा बाहु एवं मस्तक पर दंशन करने पर चतुर्गुण रूप में दुग्ध-पान का निर्देश दिया है, यहाँ विचारणीय यह है कि पुराणकर्ता ने दुग्धमात्रा का निर्देश नहीं दिया। मत्स्यपुराण में कृत्या नामक विष का उल्लेख है जिसके शमन के लिए धूमयोग का विधान बताया गया है।

आयुर्वेदीय ग्रन्थों का व्यापक रूप से अध्ययन करने के पश्चात् ज्ञात हुआ कि तद्विषयक साहित्य का स्वतन्त्र रूप से वर्णन नहीं है। परन्तु साहित्य का अध्ययन करने के पश्चात् विदित हुआ कि आयुर्वेद शास्त्र के ज्ञाता महर्षियों को विष का ज्ञान अत्यन्त प्राचीन काल से था ये वर्णन मौलिक प्रतीत होते हैं। इनमें तत्कालीन युग प्रचलित विषकन्या गर-विष तथा विभिन्न प्रकार के कृत्रिम विषों का वर्णन मिलता है। सुश्रुत संहिता के अतिरिक्त अन्याय आयुर्वेद की संहिता एवं संग्रह ग्रन्थ में विषतन्त्र का प्रसङ्ग गौण रूप से आता है। यद्यपि विषतन्त्र अथवा अगदतन्त्र आयुर्वेद के अष्टाङ्गों में एक अन्यतम अंग है।

आयुर्वेदीय अगदतन्त्र का प्राचीन साहित्य—

सुश्रुत संहिता, कल्पस्थान सम्पूर्ण

चरकसंहिता, चिकित्सास्थान २३वाँ विषचिकित्सा अध्याय

अष्टाङ्गहृदय, उत्तरस्थान ३५,३६,३७,३८ अध्याय

अष्टाङ्गसंग्रह, उत्तरस्थान ४०वाँ अध्याय

शार्ङ्गधर संहिता—यत्र-तत्र

भावप्रकाश—चिकित्सा स्थान ६७वाँ अध्याय

आचार्य चरक ने विष किसी विशिष्ट द्रव्य को नहीं माना है अपितु वह द्रव्य जिसमें लघुरक्षादि १० गुण वर्तमान हो।

विष की उत्पत्ति समुद्र-मन्थन से ही मानी गयी है। स्थावर एवं जङ्गम भेद से विष के दो प्रकार के होने का उल्लेख है। इसी परिप्रेक्ष्य में जङ्गम एवं स्थावर विष के संयोग से गर-विष की उत्पत्ति बतलायी गयी है। संहिताकार ने विष को त्रिदोषज प्रकृति के अनुसार प्रकोपक बताया है।

चिकित्सा की दृष्टि से संहिताकार ने २४ प्रकार की चिकित्सा का वर्णन किया है।

कपित्थफल पक्व तथा अपक्व दोनों रूप में विषनाशक होने का उल्लेख है।

घृत का सेवन करने से प्रायः समस्त विष-विकारों को दूर करने का वर्णन है।

विष पीड़ित मनुष्य में प्रथम विष रक्त को दूषित करते हुए फैलता है। चिकित्सा की दृष्टि से रक्तवेग को रोकने के लिए शीतल प्रदेह प्रसेक आदि निर्देश दिया गया है।

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चिकित्सा

२३वें अध्याय में सर्प के तीन भेद बताये गये हैं—(१) दर्वीकार (२) मण्डला (३) राजिमान—ये सर्प क्रमशः वात-पित्त, कफ प्रकोपक होते हैं। सर्प के दंशन होने पर लक्षणों, साध्यासाध्यता एवं विष निवारण का उपाय बताया गया है। कीटविष, उन्दुर, विष, लूताविष, वृश्चिक विष, मण्डूकविष आदि के विषों का वर्गीकरण एवं चिकित्सा का उल्लेख है। सर्प विष के लिए घृतपान का विशेष महत्व दिया गया है। दंश में सर्वप्रथम अरिष्टाबन्धन तत्पश्चात् अन्य प्रकार की क्रियाओं को करने का निर्देश है। चिकित्सा की दृष्टि से अनेक प्रकार की अगद औषधियों का उल्लेख है। इसी परिप्रेक्ष्य में यह वर्णन है कि काकांड (केवाच) के मूल के रस से पीसा हुआ तंडुलीय मूल का पान तथा लेप से समस्त प्रकार के विष दूर होता है।

सुश्रुत, माधवनिदान, भावप्रकाश तथा अन्य संग्रह ग्रन्थ लगभग चरक मतानुसार अपने अपने मत व्यक्त करते हुए विषों का वर्गीकरण तथा चिकित्सा आदि का उल्लेख करते हैं। परन्तु सुश्रुत ने शल्य-कर्म द्वारा विष व्यथा को दूर करने का कहीं-कहीं वर्णन किया है। उदाहरण के लिये—कल्पस्थान के पाँचवें अध्याय में अरिष्टाबन्धन के पश्चात् (सर्प दंश) शस्त्र कर्म द्वारा दंश स्थान को क्षत करने का उल्लेख किया गया है। सु०सु० ४५।२२८ मूत्रममानुषं च विषापहम् अर्थात् मनुष्य के मूत्र को विषनाशक कहा गया है। राजाओं पर उनके शत्रुओं द्वारा जिस प्रकार आहार द्वारा विष का प्रयोग होता था उसी प्रकार कामशक्ति के छिद्र से विषकन्या राजनीति में प्रवेश पाती रहीं। इस विषकन्या के साथ राजा जब समागम करते थे तो शीघ्र ही उनका प्राणान्त हो जाता था। (सु० क०) इसी में वर्णित है कि विषकन्या से मैथुन करने पर जननेन्द्रिय गलकर गिर जाती है और पुरुष शीघ्र ही मर जाता है।

संग्रह ग्रन्थ भैषज्यरत्नावली में अपमृमुर्षु अधिकार में जल में डूबे हुए व्यक्ति तथा ग्रीवापास बन्धन (फांसी) से श्वास रुक जाने के कारण मरणासन्न व्यक्ति की चिकित्सा का उल्लेख है।

चाणक्य ने औषधि लिप्त वाद्यों के शब्द से विष नाश की बात लिखी है। इसी परिप्रेक्ष्य में ही विषकन्या द्वारा प्रयुक्त विष के परिहार्य के लिए चाणक्य ने प्रयोग लिखा है। कुछ वानस्पतिक द्रव्यों से बनाया हुआ तेजनोदक द्रव औषधि द्वारा विषकन्या के गुप्त अंग को प्रक्षालन से और सेना पर किये गये विष प्रयोग के ऊपर इसके उपयोग से विष का असर नहीं होता।

प्रस्तुत शोधप्रबन्ध को निम्न प्रकार से प्रारूपित किया गया है। प्रथम अध्याय में परिचय, द्वितीय अध्याय में ऐतिहासिक महत्व के अन्तर्गत वेदों, पुराणों, उपनिषदों, धर्मसूत्रों, स्मृतियों का ऐतिहासिक परिप्रेक्ष्य में आलोचनात्मक अध्ययन प्रस्तुत किया गया है। तृतीय प्रकरण में आयुर्वेदीय शास्त्र में अगद तन्त्र के अन्तर्गत वृहत्त्रयी, लघुत्रयी तथा अन्य आयुर्वेदीय ग्रन्थों का अध्ययन कर तद्विषयक साहित्य उपस्थित किया गया है। तत्पश्चात् आयुर्वेद ग्रन्थों से अतिरिक्त ग्रन्थों से अगद तन्त्र विषयक साहित्य का इस शोधप्रबन्ध में समावेश है और अन्त में उपसंहार एवं सन्दर्भ ग्रन्थों की सूची दी गयी है।

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DRAVYAGUNA

STUDY ON ANTI-CANCER ACTIVITY OF *SEMECARPUS ANACARDIUM LINN. F.*

Vinod Kumar Joshi

Sup. *Dr. G. C. Pant*
Co-Sup. *Dr. P. V. Sharma*
Co-Sup. *Dr. B. L. Rastogi*

Cancer is a world-wide problem and the specific incidence rates for cancer of all sites is quite similar in most countries. Several outstanding reports have appeared in the literature on cancer epidemiology in western countries as well as from some centres from India.

Carcinoma of the cervix is the most common cancer seen among the female population over the world, but its impact is more pronounced in the developing countries. Indian women are more prone to this disease as compare to their western counterpart (Halder et al., 1955; Shanta and Krishnamurthy, 1969 and Sanyal et al., 1971). Carcinoma of the cervix forms 28.6% of all cancers and 51% of all cancers in women in India (Shanta and Krishnamurthy, 1969).

In our own institution carcinoma of the cervix constituted 30.53% i.e. 3053 cases out of 10,000 malignant cases registered and forms 50.7% out of all malignancies seen in women.

Despite the use of expensive surgical, radiotherapeutic and chemotherapeutic procedures on women with primary cervical cancers, noteworthy gains relative to survival and freedom from the disease have not occurred during past few decades, specially in advanced cancers.

In Āyurvedic literature there are certain syndromes, diseases, growths, malignant and incurable conditions are described which seem to be very much close to the cancerous conditions described in modern medicine.

The treatment of these malignant conditions has been described as Kshāra karma (application of caustics), Sastra karma (surgery) and Agni dagdha (cauterisation).

In Āyurveda *Semecarpus anacardium* Linn. f. is known as Bhallātaka which has been prescribed in malignant conditions. The drug is of plant origin and its nut contains oil is used as a remedy.

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In India as well as abroad number of scientists have reported anti-cancer activity of *Semecarpus anacardium* Linn. f. in experimental tumour system and in clinical cases of cancer.

The present work comprised four parts. The first part introduces the subject with review of literature in two sections i. e. modern literature on cancer and its treatment and Āyurvedic literature on cancer. Part two of the thesis deals with experimental studies i.e. hematinic activity, anti-inflammatory activity, anti-bacterial activity, qualitative iron test and acute toxicity study in animals.

In experimental animals statistically significant rise in hemoglobin was found in Bhallātaka treated group as compared to control group. No significant anti-inflammatory was observed in experimentally carrageenin induced inflammation in animals.

No inhibition of bacterial growth was observed in broth culture inoculated nutrient agar plates.

Bhallātaka oil contains iron as confirmed by qualitative iron test.

LD_{50} was observed to be 900 mg/kg by oral administration and 700 mg/kg by intraperitoneal administration. The clinically used maximum dose was 2 gm/day or approximately 40 mg/kg/day. It, therefore, appears that the clinically used dose was well within the safer range.

In third part observations and result with comparative clinical studies treated by *Semecarpus anacardium* Linn. f. (Bhallātaka) and Cyclophosphamide (standard drug) in eighty cases of cancer uterine cervix are presented and discussed.

In clinical patients symptomatic improvement in the form of control in per-vaginal bleeding, veginal watery discharge, pain in lower abdomen and back etc. were found in both Bhallātaka-treated and cyclophosphamide-treated group.

Sense of well-being was found in almost all the cases in both the groups. But significant increased appetite and weight was recorded only in Bhallātaka treated group.

Similarly hemoglobin was found raised in Bhallātaka-treated group in about 80 % cases, while none was found with increased hemoglobin in cyclophosphamide-treated group.

Regression of growth was much more marked nearly 70% in Cyclophosphamide treated group, while in Bhallataka-treated group it was only 35%.

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In Bhallātaka-treated group toxic manifestations were much less as compared to cyclophosphamide treated group, where nausen and/or vomiting, a opecia and mild cystitis were not.

In Bhallātaka-treated group epigastric burning and itching were reported in ten cases which were ameliorated by administration of ghrita with milk and coconut.

Finally in part fourth discussion, summary and conclusion and the list of consulted reference are given.

In conclusion, *Semecarpus anacardium* Linn. f. appears to be a promising and ideal drug for malignant growth conditions without any major toxicity and as it does not need hospitalization for the treatment.

By modern study it has also become clear that there is an increased incidence of tumour in human with immunodeficiency (Allison, 1976). Looking to this, *Semecarpus anacardium* Linn. f., on one side, destroys the disease and on the other promotes the strength of the patient (immunity). it may be an ideal drug with a promising future. In modern medicine there is no drug like *Semecarpus anacardium* Linn. f. which combines both the above properties.

EFFECT OF SOME INDIGENOUS DRUGS ON CHYLURIA

Bhagawan Singh Sup. *Dr. J. K. Ojha*

Prameha has been established as single dominant urinary disorder among the lower tract manifestation. Since entire homeostasis is governed by Tridosh, vitiation of any three components will always have its manifestation over a particular organ or system. Same has been found true in Prameha which has resultant in twenty types of Prameha out of which ten are Kaphaja, six are Pittaja and four are Vātaj.

Two ancient laureats of Ayurvedic system of medicine have emphasized that vitiated Kapha located in the Vastipradesh gives rise to Kaphaja Prameha which has its varied manifestation. Passage of rice milky water urine has been described by Charaka as Suklameha whereas Sushruta, Vāgbhatta have considered a similar presentation by the name Pista Meha. In modern medicine this condition has been designated a chyluria and carter for the first time in 1862 described the pathogenesis where he demonstrated rupture of dilated lymphatics into the pelvis due to blocked

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thoracic duct. Mckenzie in 1882 demonstrated pyeloymphatic fistula in a post mortem study on a patient who died with a filarial chyluria. Wuchrer in 1868 demonstrated microfilaria in a chylous urine and the subsequent demonstration of adult filarial larva in the inguinal lymphatics as well as common iliac lymph node generated a concept of lymphatic backflow resulting into pyelo-chylous fistula. In modern medicine association of elephantiasis with filariasis is a known complication in all the tropical countries. This fact has been described by Sushruta that "in those countries where ditches and ponds are filled with water and are moderate cold prevails Shlipada is founda is found specifically". (Su. Ni. 12/14).

Charaka has considered such climate falls under costal region and bank of those rivers which are full with stream in all the seasons. (Cha. Ka., 1/10).

These two epidemiological observations are the strongest supporting view that mosquito born disease specifically in Kapha prone individual results in a condition what has been known in Sanskrita as Shlipada (Cha. Chi., 12/98).

As a part of pathogenesis is quite possible that repeated inflammatory response in the inguinal lymph nodes leads to distal obstruction of lymphatic flow. Since Prameha is also Kapha dominated disease, a etiological similarity between the two conditions are quite like'y to result in the obstruction of lymphatics. The anatomical description of Vasti Pradesh has not been well understood as it has been described by modern anatomists in specific relation with lymphatic system and its relation with chyluria. As it is evident by Charaka (Cha. Chi., 6/5) that Kapha located in hypogastric region vitiates muscle, intravascular compartments and alters the metabolism of lipoprotein. Its very likely that this obstruction is taking place in the common iliac and hypogastric lymph node which is specifically blocking or producing non-specific inflammatory response in perihilar lymph nodes of kidney resulting in chyluria. Interestingly Shlipada is a least common observation among chylurics which favours of possibility that the site of obstruction in Shlipada is mainly inguinal group of lymph node where as non-inflammatory response in the coeliac and iliac group of lymphatics results in diversion of lymphatics in to the urinary space.

The above ideas have been conceived as a part of present research work and we have tried to explore the possibility of two indigenous drugs which has been used in ancient time for the conditions due to vitiation of Kapha like elephantiasis. Shākhotaka and Manjisthā both the plants have been given a worthy recognition in the Dravyaguna as anti-Kapha drug in a non-specific disorder of urinary tract.

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These two drugs with a placebo study has been evaluated on the known modern scientific and laboratory parameters to stand its validity in the modern context.

The important features of Pistameha which has more similarity with chyluria are given below :

(i) Chyluria and Pistameha are a Kapha dominant presentation.

(ii) The colour of the urine is similar in both diseases, like rice water.

(iii) All the chylurics have similar symptomatic presentation as described in Pistameha i. e., rice water in appearance, excessive in quantity, cold, concentrated and produces excitement during act of micturation.

So far no single or combined drug has been recommended in Āyurvedic literature to the treatment of chyluria, however, a similar causative agent of chyluria in modern medicine that is filariasis has similarity in the presentation of elephantiasis or filarial orchitis. For this disease the name Shlipada has been coined by Charaka Samhita where Shākhotaka (*Streblus asper* Lour.) has been used as antifilarial drug in almost all of the Chikitsa Granthas, whereas Manjisthā (*Rubia cordifolia* Linn.) has been used in Charaka for the management of Prameha by their antagonistic properties of Kapha prone chyluria that is Ushna in Virya, Tikta in Rasa and useful in urinary discharges.

Thirty-two patients of chyluria were studied in detail. Each patient was studied with reference to his age, sex and a detailed present, past, personal and family history, routine urological blood investigations included urinalysis, blood urea, serum cholesterol, serum protein, urographic studies, retrograde urogram were studied and renal biopsy was done only in 25 per cent patients.

Only about 60 per cent patients presented in the month of July. Fever with chill or without chill were seen in most of the patients (50%). Vericose vein was seen in lower per cent of the patients (31.25%).

Only 28.13 per cent of the patients had a haemoglobin between 6-10 gm%. Eosinophil count was insignificantly raised in 31.25 per cent of the cases. Majority (56.25%) of the patients had moderate renal insufficiency which was shown by his blood urea in the range of 40 to 80 mgm%. Hypoproteinaemia was observed in 62.5 per cent patients. Looking at the range and standard deviation it was observed that serum cholesterol decreases to a significant value than triglyceride. All the chylurics were

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found to have nephrotic range proteinuria in the range of 3 to 10 gm in 24 hours with significant lipiduria especially triglyceride and phospholipids.

Maximum proteinuria was 30gm/24 hours and minimum was 3gm/24 hours. The mean value of serum protein of chylurics was 4.59gm% whereas 6.83 gm% in controls. Maximum triglyceride was 12660 mg/24 hours and minimum was 2244 mg 24 hours, maximum phospholipid was 504 mg/24 hours of urine and minimum was 54 mg/24 hours. Endoscopy examination was conducted only in seventeen patients. 52.35 per cent of the patients showed chylous efflux from right side, 17.64 per cent showed efflux from the left side and in 29.41% of the patients it was bilateral. Vascular impression were seen in 83.3 per cent of the patients on retrograd pyelography. Majority had normal function (83.3%) on excretory urography. H. stological observations were done only in eight patients out of which three were increased mesangial matrix, two were found to have minimal change glomerulonephritis and three had focal proliferative changes.

Out of total thirty two patients, twenty were kept on single drug whereas twelve patients were prescribed a combination of Shākhotaka (*Streblus asper* Lour.) and Manjisthā (*Rubia cordifolia* Linn.) for a period of 3 weeks. Same patients were taken as control prior to therapy. Haemoglobin level was improved upto 13.01 gm% against a control of 12.17 gm%, by a single drug therapy (*Streblus asper* Lour.) whereas it was improved upto 13.62 gm% against a control of 12.40 gm% by combined therapy (*S. asper* + *Rubia cordifolia* Linn.). Serum protein improved from 4.58 gm% to 5.94 gm% by combined drug therapy, and from 4.60 gm% to 5.78 gm% by single drug therapy. Serum cholesterol value by single drug therapy was observed to be highly significant ($P < 0.001$) while it was of no significance change in serum triglyceride pattern ($P > 0.05$). By use of combined therapy both serum cholesterol and serum triglyceride level improved significantly (P value of serum triglyceride < 0.05, P value of cholesterol < 0.05). In nephrotic range of proteinuria there were significant improvement by single as well as combined therapy ($P < 0.05$). There were appreciable reduction in lipiduria (both triglyceride and phospholipid by single drug therapy while by combined drug therapy significant change was observed only in triglyceride value but not in phospholipid value.

The humble beginning of this research project is a tiny effort to establish these two Indian medicinal plants (*Streblus asper* Lour. and *Rubia cordifolia* Linn.) to be used and recognised for the treatment of chyluria. The formulation of doses have been done in accordance with Āyurvedic concept and they have been shown to be beneficial than the

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placebo group. Available modern investigative parameters have supported the notion that our ancient drugs are equally competent to deal the medical problems as well as their easy preparation and nontoxic nature is an edge over the modern medicine.

According to Āyurveda the drugs of Tikta Rasas are effective in Kaphaja disorders particularly when it is of obstructive in nature. Both Shākhotaka and Manjisthā belongs to this group and exert their effect by dint of their prominent Tikta Rasa. Tikta is composed of Vāyu and Ākash Mahabhutās out of which Vāyu is due to its roughness, dries up and absorbs the Kapha material which obstruct the channels in which Ākash Mahabhuta further helps in the process.

Thus there is a promising scope of Shākhotaka and Manjisthā to be used in established chylurics and there is strong suggestion that these drugs may be tried in further Kapha disorders because Charaka has declared that "One who knows the names and morphological characters of the drugs and also their therapeutic uses is said as expert of them." This work throws a new light on the properties and uses of the drugs under study particularly in respect of chyluria and it is also a new contribution in the field of Dravyaguna.

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KAYACHIKITSA

A CRITICAL STUDY ON THE CONCEPTS OF MENTAL HEALTH AND ITS PROMOTION

Pramod Kumar Bondriya

Sup. *Dr. R. H. Singh*
Co-Sup. *Dr. Ratan Singh*

The present thesis aims to undertake a critical study on the concepts of mental health and its promotion as described in ancient scriptures in the light of current thought on the subject. It is widely understood that the ancient literature conceives a high mental and spiritual model of mental health and wellbeing. Accordingly it is considered that the ancient Indian texts advocate a number of methods and practices to preserve and promote the mental health and to improve it qualitatively to an infinite level leading to a supermind.

It is also a fact that there has been a mental health crisis throughout the world in recent years. This mental health crisis is now often attributed to the modern way of living with industrial development and urbanization which have pushed the mankind greately away from the nature. The man living in his changing environment is facing the crisis of adjustment and adoptation which has threatened his wellbeing. This fact is now well taken by the health planners and policy makers. Obviously there are attempts to develop means and measures of promotion of mental health. At this juncture, it appears advisable to derive wisdom from the ancient insights as found in the scriptures. Hence, it is essential, to workout with greater clarity the mental health models and the methods of its promotion, prescribed therein, so that the ancient insights may be utilized and exploited for devoloping models for meeting the present day mental health crisis.

It is with this objective that the present work was undertaken.

Recent surveys have shown that mental disorders are on the increase and at the present rate of increase of mental disorders are moving towards a point where society will be unable to cope with number of patients in need of treatment. Mental disorder is becoming principal mass disease of our times and therefore, it is becoming urgent to deal with it at all levels including research in the field of concepts of mental health and its promotion.

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Mental health should not be viewed separately from physical or social wellbeing. Different aspects of mental health development should not be separated artificially but integrated into a holistic approach. Improvement in physical health will improve psychological functioning and is likely to reduce psychological hazards. Mental health is equally important in socio economic development of a nation and stability of all the nation with each other.

Mental health should have high priority in research and its application because mental disorders may presage unproductive lives. Mentally ill persons may perform poorly as parents so that their children will be born into a condition of severe deprivation and run a high risk of mental disorder.

A vast amount of Āyurvedic and ancient Indian knowledge about mental health remains unused; and its application might substantially improve the fate of all human beings. Action directed to the promotion of mental development and health would lead to overall development.

We all need continuous health more than anything else, but, generally we do not desire it more than other desires.

In pursuit of the goal of health for all by the year 2000 A. D. and national health policy of health for all, it was thought desirable to focus our research study on the most valuable and comparatively least worked, researched field of total hea'th i. e. Mental health. The concept of mental health is not clear to the current workers. So due to the lack of a clear concept of mental health, modern workers do not have a clearcut goal of promotion and prevention. Ancient Indian literature is full of mental health promotive ways and measures of prevention. With the aim of finding a clear concept of mental health and ways to achieve this goal the present study was launched.

The issue of giving importance and priority to the promotion of mental health and primary prevention of mental disorders, generally generates disagreement. It is generally argued by persons in the field of public health and psychiatry that problems of infections diseases, malnutrition and psychiatric illnesses are so great and the needs for clean water, sanitation, maternity services, treatment of physical and psychiatric illnesses are so pressing that it is premature to provide services for promotion of mental health and primary prevention of mental disorders. Some argue that mental illness is not itself a significant problem. Such as an assumption is however no longer tenable and the public health problem posed by mental disorders has been widely recognized in recent years. The extensive harm-

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ful consequences which result from the failure to provide adequate mental health promotive and mental disorder preventive measures is also becoming clear. Those who suffer from mental disorder they function at far below their optimal level, which causes an unnecessary burden on the community as well as personal distress.

Āyurveda considers mental health or wellbeing as the part of total health. According to Āyurveda '*Āyu*' i. e., life is a composite entity consisting of the physical body, the mind, the senses and thd soul. A balanced harmonious functioning of these four components is the basis of health and the reverse is the ill health. Mind has been considered to possess three dimensions with '*Rājas*' '*Tāmas*' on the two extremes and their balance being called the '*Sātvika*' state. Depending upon the relative preponderance of the above mentioned qualities of mind, the mental health and mental abilities of an individual are determined. Āyurveda has discussed in detail, the characteristics of mental health in the context of *Prakṛti* and *Satva Parīkṣā* etc. The measures of promotion of mental health by *Sadvṛtta*, *Ācāra*, *Medhya Rasāyana* and *Yoga* appear to have been given due emphasis.

The aim of the present study is to undertake a critical study on the Āyurvedic and ancient Indian concept of mental health and its care and to examine its relevance in modern times. This study consist of the following components :

1. A critical literary survey of Āyurvedic texts and other ancient scriptures in order to work out the ancient Indian model of mental health and its care.
2. A study of the current modern concept of mental health and its care—promotion and prevention.
3. Attempts to correlate the ancient and modern concepts of mental health and its promotion.
4. Evaluation of the ancient concepts of mental health and the principles of its care in the light of modern science.
5. Evaluation of various ancient and current mental health movements, their ideologies and relevance in present times.

Healthy mind is most important for human life, and its promotion for further health improvement is necessary. But every little work has so for been done in the scientific field of mental health to reach a clear concept, methods of promotion and measures for primary preventive care. In view of a rapid increase in the incidence of mental disorders and looking to the rich Āyurvedic concepts about the mind, its improved states and the ways

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of promotion of mental health, it was considered useful to launch this conceptual study to evaluate critically the current literature. Āyurvedic and ancient Indian literature related to the concepts and criterion of mental health and its promotion and primary preventive care.

This conceptual study is dealt in ths present thesis under the following heads :

1. Current concepts of mental health and its promotion.
2. The trends of mental health movement.
3. The ancient concepts of body and mind.
4. The ancient Indian concept of mental health.
5. The ancient Indian methods of promotion of mental health.

Thus from the present study it can be concluded that :

(1) The very fact that many difinitions on mental health are given by different authors, as reviewed in this work shows that there is no agreement on what is mental health in the modern literature.

(2) Mental health as conceived in Āyurveda and other Hindu traditions is a dynamic process and is dealt in relevance to the four dimensional concept *Āyu* i. e. life namely physical, sensorial, mental and spiritual. On the basis of critical study of the Āyurvedic texts, we have identified two distinct models of health conceived in Āyurveda namely, 1. Total Health and 2. Absolute Health which are discussed thoroughly in this thesis.

(3) The ancient texts describe a number of medicinal and non-medicinal measures for promotion and primary prevention in mental health namely *Sadvṛtta*, Rules of good conduct for pregnant woman (for her and for the wellbeing of foetus), Mental health care of the child, *Dhāraṇīya* Vega, *Ācāra Rasāyana*, *Medhya Rasāyana*, *Yoga* including *Yama Niyama* etc. These if followed truthfully can solve interpersonal human problems and soical tensions.

(4) However, the scope of mental health has been defined as prevention of mental illness and promotion of mental health. Within prevention three levels of prevention of mental illness are mentioned. However, precise cause of mental illness is not yet known, therefore, basic primary prevention of mental illness is not possible,

The cause of certain physical diseases, which are on the increase in the modern industrialized and urbanized world, is known in the form of psychological stress. This type of cause of ill health had been prevented in ancient Indian culture by practice of various kinds of yoga and other

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measures developed for positive health, while the modern systems of medicine are only recently, yet insufficiently trying to grapple with this cause mainly psychological stress. This also explains the reason why in industrialized west today there is increase of various kinds of mental health promotive movements.

(5) A study of trends of activities in the field of promotion of mental health indicates that the following mental health movements are in progress world wide viz.

(i) Classical yoga movement,

(ii) Ancient Indian medicines movement,

(iii) Ideological and religious movements,

(iv) Transcendental meditation movement,

(v) The rational yoga movement and similar other activities.

(6) Regarding promotion of mental health the materialistic west has not yet discovered or evolved any standardized means of promoting mental health. It is only in the ancient Indian culture that many such means have already been standardized in the form of various religious life styles such as : Path of Buddha and the three main paths spoken by Kṛṣṇa to Arjuna to be pursued by the recepient according to the temperament.

(7) In view of the growing significance of mental health, there is a need of launching programms for evaluation and spread of the ancient methods of promotion and prevention. As these methods have been in use for centuries they may be utilized now without waiting for data to validate their use because research and evaluation of these methods on scientific parameter will take its own course.

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RASA-SHASTRA

STUDY ON UPAVIṢAS WITH PARTICULAR REFERENCE TO DHUSTUR

V. N. Sharma

Sup. *Sri S. P. Sen*
Co-Sup. *Dr. D. Joshi*

Ayurveda or science of life deals with prevention and cure of diseases by all possible means and measure. These include administration of drugs to cure diseases, physical and mental exercises for maintenance of strength and vitality to ward off diseases as also for ensuring tranquility of mind to keep the biological system, inclusive of body and mind, in perfect order. According to Ayurveda anything which is available on the surface of the earth can be used as medicine. These may be such products, which are free from toxicity as also those, which ordinarily act as poisons. These poisonous materials are classified in Ayurveda as visas and upavisas, according to severity of toxicity. In fact these visas and upavisas occupy a very important place in Ayurveda especially in Rasa-Shastra. It may be mentioned that the term 'Rasa' refers to 'Mercury' or 'Mercurial', which are toxic or poisonous in nature. In Ayurveda, the use of the word 'Rasa' is extended further to all such items which possess toxic property but still can be used in medicine. The visas and upavisas of Ayurveda belong to this category of poisonous materials which possess invaluable therapeutic properties. The Rasa Vaidya and exponents of Rasa-Shastra however advocated the use of these visas and upavisas in medical practice, after subjecting them to such treatments, which are known as shodhana.

The upavisas, in particular occupy an important position in Ayurvedic therapeutics. Besides their use in clinical practice, they play dominant role in pharmaceutical operations, especially in preparing heat resistant clay made casserols, and used as adhesives or pastes to plaster the joints of earthen vessels, for solidification of mercury and also for shodhana of sulphur and mercury. Another important property of upavisas is that they activate the basic materials and enhance their medicinal values. Earliest record about upavisas dates back to 10th century A. D. which is very much the period, when Rasa-Shastra made its headway in the field of medical science in India. It is apparent from "Kautilya Artha Shastra" that the knowledge of Rasayan, involving the use of upavisas in the preparation of Siddha Swarna (Gold), started sometimes after 325 B. C. The use of metals in the form of minute subdivision and in fractional doses seems to have been in vogue in south India at near about the same period.

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It may be said, that although the knowledge of visa dates back to prehistoric age, its actual documentation and descriptive narration seems to have taken place for the first time during the period of "Kautilya Arth Shastra" (325 B. C.). But the use of visa in the earlier period seems to be restricted to homicidal purposes as is evident from the historical records of the use of "visa kanya", "visa garbhit sura", visadushit jal" etc for the purpose of killing enemies. In the treatise, written by Carak, Susrut and Bagbhatta, the classification of only Visas and their toxicological symptoms alongwith the treatment measures against the effects of poisoning have been detailed but no elaborate description about upavisas is to be found in these texts. The effect of season and climate on the properties of visas and upavisas are however mentioned in later texts. The detailed description about their toxicological properties and pharmacodynamic actions are lucidly described in the texts, which are devoted mainly to Rasa-Shastra. These and other historical records show that Rasa-Shastra had emerged as an out-come of researches by Siddha sampradaya and more especially as a result of the development of Tantra Siddha. Evidences are on records that introduction of upavisas into therapeutics started only after development of Rasa-Chikitsa because description of upavisas appears to have been recorded for the first time in Rasa-vangmaya. The number of materials termed as upavisas varied from period to period and starting with five materials mainly Ark, Snuhi, Dhatur, Karbir and Langali in the initial list of upavisas, it extended gradually up to eleven plant products including Sunhi, Ark, Dhatur, Karbir, Langali, Visa musti (Kuchila), Bhanga, Bhallatak, Gunja, Ahiphen, and Jaypal. It is found that development of upavisas depended upon their wide application in therapeutics and had been associated with the development of sciencc of Rasa-Shastra. Review of literature shows that there have been regular reviewing of the pharmacological activity pharmaceutical uses and therepeutic application of the various upavisas. Ayurvedic Samhitas eg. Caraka Samhita, Susruta Samhita, Rasa Samhita and other treatise eg. Rasaranava, Rasachikitsa, Rasaratna samucchya, Rasa pradipika, Rasatarangini have made different claims about the potentiality of the various upavisas. An analysis of this shows that only three items i. e. Dhatura, Karbir and Langali have been recognised as upavisas of positive medicinal value in all the classical texts. The review of the Ayurvedic texts establishes one common fact that upavisas need be subjected to preliminary treatment known as shodhana to reduce their toxicity and increase their therapeutic merit. This aspect has been completely ignored by the modern medical scientist and that is why these drugs, ever with their great therapeutic potentiality find limited application in medical practice.

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Ayurvedic texts indicate that Dhatur is most widely used upavisa in Ayurvedic medical practice. Studies on upavisas has, therefore, been concentrated on Dhatur as a representative of the group of plant products, designated as upavisas in Ayurveda.

This study includes experimental study on the pharmaceutical operation prescribed in Ayurveda for shodhana of Dhatur, Chemical analysis of crude and shodhit Dhatur to estimate the changes in chemical property, if any, brought about by shodhana, relative toxicity of the crude and shodhita Dhatur and comparative evaluation of their pharmacodyanamic properties.

In the pharmaceutical study, two of the prescribed methods have been employed, one in which drug (Dhatur seeds) is treated with boiling cow's milk and other, in which the drug is treated with cow's urine. In the absence of specific instructions, having been laid down about the details of the procedures, some standards had to be worked out in the pharmaceutical operations. The text (Rasatarangini) suggests swedan of the seeds of Dhatur for one yama, which had to be deciphered as treating the drug with boiling cow's milk or cow's urine for three hours instead of exposing the drug to the vapours of cow's milk or cow's urine. This innovation had to be done because exposure the vapour of cow's milk or cow's urine would only mean exposure of the drug to water vapour, emanating either from milk or from urine. The period of three hours had to be resorted to, on an analogy that a full day period of 24 hrs is considered to be composed of eight yamas. The products obtained by the two methods on physico-chemical examination showed some variation. In regard to physical property, cow's milk treated product showed an inerease in weight with slight bulging of the seeds. The urine treated product on the other hand had a reduction in weight without any change in shape and structure of the seeds.

The chemical analysis showed that urine treated sample had a lower percentage of alkaloid than the original crude material and the T L C pattern indicated production of artifracts probably due to hydrolysis of the alkaloids. In the case of milk treated product there was an apparent increase in alkaloid contents and T L C picture showed some faint additional spots for basic constituents, presumably due to incorporation of basic components, derived from milk protein.

The alcoholic extract prepared with these drug samples in soxhelet extractor by hot continuous extraction method were dried and used for experimental biological studies to evaluate relative toxicity and pharmacodynamic property.

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The toxicity studies carried out on frogs revieled the following :

The intraperetoneal injection in the graded doses of aqueous suspension of alcoholic extract shows that the drug produces mild to severe sedation and red or purple spots on localised area all over the body according to degree of toxicity in individual drug preparations. A does of 1.5 ml aquous suspension with alcoholic extractive of crude Dhatur (=750 mg) of drug was found lethal, killing all the animals within 3 hours and after 2½ hours. The same dose of aqueous decoction (1.5 ml) of extratives of the two shodhit products were found to produce only slight sedation without lethality. A dose of 2.5 ml of aqueous suspension of the alcoholic extractives of the shodhit preparations (=1.25 gm of the drugs) however, proved to be lethal in both the cases. Examination of the effect of three drug samples on cardiac activity of frog showed that while the crude Dhatur preparation in a dose of 100 mg caused extreme cardiac irregularity, followed by arrest of heart in diastole, the milk treated Dhatur and urine treated Dhatur had only but slight reduction in force of contraction in this dose. In the case of milk treated Dhatur a dose of 200 mg caused cardiac irregularity, associated with increased contraction and extra systoles, followed by cardiac arrest in systole. The urine treated Dhatur, on the other hand showed an initial inhibitory effect on cardiac activity in the dose of 200 mg, which was followed by gradual recovery of both rate and force of contraction of heart. This suggested that Cow's Urine treated shodhit product is much less toxic than both crude Dhatur and Cow's urine treated shodhit Dhatur. This was confirmed in the toxicity study carried out in albino rats. In the first set of experiments a dose of 526 mg of crude Dhatur was found lethal to all the 15 animals under study, showing signs of resperitory failure, difficulty in deglutination and intense depression of central nervous system. A dose of 804 mg of Cow's milk treated shodhit Dhatur was found lethal to 15 animals, death occuring due to respiractory failure. The death of animals however, occured at a period of 15 hours after the administration of drug while in case of crude Dhatur death occured at the end of two hours only. The Cow's urine treated Dhatur, when administered in a dose of 634 mg did not cause any lethality even upto a period of 24 hours. There was only slights sedation followed by some irritational effects observed during this period.

The drug Dhatur, having been reported in Ayurvedic texts to be useful in fever, the antipyritic effects of the three drug samples were estimated in experimentally induced hyperpyrexia by TAB injection in albino rats. The effect of the drugs were examined by measuring the

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rectal temperature at 30 mts and 1½ hrs time intervals and compared with the effect of the standard antipyrectic agent "Paracetamol".

The results substantiated the argument that shodhana of the drug Dhatura, belonging to the group of upavisas, reduces the toxicity but at the same time retains the therapeutic potentiality of its antipyretic effect. The reported analgesic action of Dhastura and the observed C.N.S. depressant action of crude and milk treated shodhit Dhastura, as well as that of Cow's urine treated shodhit Dhastura, was examined in a set of experiments by the method of Devies Ravintos and Walpole (1946).

This study showed that urine treated shodhit Dhatur, which is comparatively less toxic than crude and milk treated shodhit Dhatur and possesses a more potent antipyretic effect, failed to show any analgesic action while this property is found present in the other two samples.

The next set of experiment was designed to see if the process of shodhana affects in any way parasympatholytic activity of the drug Dhatur. The study was conducted on isolated smooth muscle the tissue into study, preperation, using rats ileum and with acetylcholine as spasmogen. Studies have shown that the antispasmodic effects of crude Dhatur is definitely reduced by the processes of shodhana. The spasmodic effect of 10 u gm of acetylcholine is blocked by a dose of 5 mg, of crude Dhatur while larger doses, such as 40 mg and 80 mg of Cow's urine treated shodhit Dhatur and Cow's milk treated shodhit Dhatur respectively were required to block the response of 10 micro gms of acetylcholine. It is of interest to see that cow's urine treated Dhatur, devoid of any analgesic action, has a better antispasmodic effect than milk treated shodhit Dhatur.

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MEDICINAL CHEMISTRY

CHEMISTRY OF NATURAL PRODUCTS

Rakesh Maurya Sup. *Dr. A. B. Roy*

Isolation and characterisation of the phenolic constituents of *Pterocarpus marsupium* Roxb

Pterocarpus marsupium (Leguminosae) is a big tree and its heartwood and bark are used in the treatment of diabetes in the traditional system of medicine in India. Systematic fractionation of different exteractives of the heartwood and branch bark of this plant resulted in the isolation of fourteen phenolic compounds including marsupsin, a new benzofuranone flavonoid, pterosupol, a new C_6-C_3-C_6-phenolic and pterosupin, a C-glucoside of a B-hydroxydihydrochalcone.

Marsupsin, $C_{16}H_{14}O_6$, m.p. 195°C. $[\alpha]_D$-4° (MeOH), exhibited a UV spectrum comparable to that of phloroacetophenone and a IR spectrum which showed bands at 3440, 3380, 1680, 1600 cm^{-1} indicating the presence of both hydroxyl and carbonyl functions in the molecule. The phenolic nature of marsupsin was revealed from the observed bathochromic shift of its UV maxima in presence of dilute alkali. Marsupsin gave a triacetate on treatment with acetic. anhydride in presence of sodium acetate and a trimethyl ether on methylation with ethereal diazomethane. The ^1H NMR spectrum of the methyl ether indicated the presence of one benzylic methylene group at 83.10 (2H,*s*), one aliphatic methoxyl group at 83.26 (3H,*s*), three aromatic methoxyl groups at 83.73, 3.83 and 3.85 (3H,*s* each), two *meta*-coupled aromatic hydrogens at 85.89 and 6.06 (1H,*d* each, J=2Hz) and four aromatic hydrogens of a 1, 4-disubstituted phenyl nucleus at 86.71 and 7.15 (2H,*d* each, J=8.8Hz). Absence of any aliphatic methoxyl group in the ^1H NMR spectrum of the parent molecule and its formation under the reaction condition indicated that marsupsin bears an aliphatic hydroxyl group adjacent to an electron withdrawing group. Based on these observations and the fact that marsupsin bears in its molecule an isolated benzylic methylene group, it was assumed to have the relatively rare 2-hydroxy, 2-benzyl benzofuranone structure. Such an assumption gained credence from its mass spectral data which showed two important ion peaks m/z 195(*a*) and 107(*b*) formed by facile benzylic cleavage. The fragment ions corresponding to the above two peaks appeared respectively, at m/z 223 and 221 in the mass spectrum of its trimethyl ether, indicating

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that the lone methoxyl group present in marsupsin is in ring A. The exact position of the methoxyl group in ring A was settled by use of appropriate UV shift reagents and from the negative Gibbs test shown by the compound. Marsupsin was thus formulated.

Chemical evidence in support of the structure VII was provided by acid catalysed conversion of trimethyl marsupsin to the aurone which was found to be identical with 4,4', 6-trimethoxyaurone, prepared from phloroacetophenone by standard procedure.

Pterosupol $C_{15}H_{16}O_3$, m. p. 158°C, U_{max} 3420 cm^{-1}, gave on acetylation a triacetyl derivative indicating that all the oxygen functions present in the molecule are hydroxyls. The structural feature of the molecule was fully disclosed from a study of the ^1H NMR spectrum of the triacetate which indicated the presence of eight aromatic hydrogens of two identical 1,4-disubstituted phenyl nucleii at 87.17 and 7.00 (4H,*d*, each, J=8Hz), two identical benzylic methylene groups at 82.84 (4H,*d*, J=6.9Hz) and one carbinyl hydrogen at 85.26 (1H, quintuplet, J=6.9Hz) in addition to the presence of two phenol acetates at 82.27 (6H, *s*) and alcohol acetate at 81.93 (3H, *s*). Based on these observations, pterosupol was formulated, which is consistent with its mass spectral data.

Pterosupin $C_{21}H_{24}O_{10}$, m. p. 167°C, $[\alpha]_D$ +108° (MeOH), U_{max} 3400cm^{-1}, was recognised to be a glycoside from its solubility in water, its paper chromatographic behaviour, high oxygen content in its molecule, and from the presence of seven aliphatic oxycarbons in its ^{13}C NMR spectrum. The resistance of the compound to acid hydrolysis and the absence of any ketal carbon in its ^{13}C NMR spectrum indicated the presence of a C-glycosyl linkage in pterosupin which was confirmed by ferric chloride oxidative cleavage of the molecule to yield glucose. ^1H NMR data indicated the presence of two *ortho*-coupled aromatic hydroges at 87.86 and 6.42 (1H, *d* each, J=9Hz), four hydrogens of a 1,4-disubstituted phenyl nucleus at 87.05 and 6.71 (2H, *d* each, J=8.4Hz), three hydrogens of -CO-CH_2-CH(OH)-Ar system as an ABX pattern at 85.21 (1H, *dd*, J=7.7, 5.5Hz), 3.36 (1H, *dd* overlapped with other signal) and 2.88 (1H, *dd*, J=14.3,7.7Hz) and an anomeric hydrogen at 85.01 (1H, *d*, J=9.7Hz). Based on these observations pterosupin was formulated as C-glucoside of β-hydroxydihydrochalcone and the positions of hydroxyl groups and of the sugar residue were settled with the help of appropriate UV shift reagents.

While the structure elucidation work of this compound was in progress, a paper describing the isolation of a compound having the same structure from the root heartwood of *P. marsupium* appeared (*Z. Natur-*

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forsch, 37c, 145, (1982) and it was designated as pterusupin by the authors of the paper. Our compound was found to be identical with pterusupin by direct comparison.

Selective methylation of quercetin

The product of methylation of quercetin with dimethyl sulphate in presence sodium acetate in refluxing acetone was characterised as 7, 4'—dimethylquercetin from detailed spectral analysis.

Isolation of hordenine from the whole plant of *Desmodium floribundum*

The alkaloid isolated from *D. floribundum* was characterised as hordenine hydrochloride from spectral analysis and direct comparison with an authentic sample. This is the first report of isolation of this alkaloid from *D. floribundum*. The formation of the alkaloid salt might be effected due to extraction with chloroform.

Tentative structure proposed for the major alkaloid of *Erythrina corallodendron*

From a detailed spectral analysis including decoupling experiments the major alkaloid isolated from the leaves of *E. corallodendron* was considered to have the same structure as that of erythristemine. Paucity of the materia' and non-availability of a reference sample precluded arriving at a definite conclusion about its structure and stereochemistry.

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FACULTY OF MEDICINE

BIOCHEMISTRY

BIOCHEMISTRY OF A NEW BACTERIOPHAGE MB 78

Javed Zafar Siddiqui Sup. *Dr. M. Chakravorty*

Section I

In this introductory section a review of the relevant literature in the areas in which investigations have been carried out, has been presented. Since the work presented in this dissertation mainly deals with the characterisation of a new bacteriophage of *S. typhimurium*, a brief review regarding some of the known phages of *S. typhimurium* has been presented. Moreover, the last part of dissertation deals with the purification and properties of phage MB78 and P22 induced lysozyme; a review of the literature on other phage induced lysozymes has also been presented in this section.

The review has been followed by a brief statement on the scope and object of the present investigation.

Section II

This section deals with the sources of the materials used in the present investigations and the methods used in general for carrying out the present studies.

Section III

This section deals with the physical and biochemical characterisation of phage MB78 which is morphologically, serologically and physiologically unrelated to the well known *Salmonella* phage P22. The new phage has a long, noncontractile tail. The ratio of protein to DNA in phage MB78 is 1 : 0.88 as compared to 1 : 1.03 for P22. This shows that the protein content of MB78 is more than that of DNA. This may be because MB78 has a long tail. The latent period of MB78 is much shorter than phage P22 although MB78 infected cells take longer time to lyse than P22 infected cells. It appears from the preliminary investigation that MB78 may contain more structural protein than P22. Further experiments are to be carried out before these assumptions could be confirmed.

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The development of phage MB78 is very much sensitive to the chelating agents—citrate and ethylene diamine tetra acetic acid (EDTA). This show that MB78 requires some divalent cations which is not necessary for either the host or the phage P22 development. The most striking feature of this phage is that it does not grow on rifampicin resistants of *S. typhimurium* (*rif* 39), which contains an altered RNA polymerase (Hong *et al*, 1971). P22 grows normally on *rif* 39 cells even in the presence of rifampicin. MB78 gives a small burst in rifampicin sensitive host—LT2 in the presence of rifampicin, if the antibiotic is added ten min after infection. The development of P22 is completely inhibited in this case. Snyder (1972) also reported that the rifampicin resistant mutant of *E. coli* (Rif R 2) does not support the development of phage T4 and λ. This suggests that like T4 and λ, MB78 too, requires the rifampicin sensitive subunit of the host for its DNA replication. Phage T7 grows normally in such mutants as it can use the host polymerase (rifampicin resistant one) of early transcription and later syntheses its own DNA polymerase (Snyder, 1972).

Section IV

This section deals with the characterisation of phage MB78 DNA at the molecular level. Digestion of the DNA with DNase I and S1 nuclease shows that the genetic material is double-stranded DNA as it is susceptible and resistant to DNase I and S_1 nuclease respectively. Moreover, unlike λ and like P22, MB78 DNA does not have any sticky ends. Digestion with exonuclease III and reannealing experiment shows that like P22, MB78 DNA is also terminally redundant. EcoRI and Hpa I restriction endonuclease digestion pattern of phage P22 and MB78 DNA shows that the genomic make up of the two phages are quite different. This was confirmed by DNA-DNA hybridisation experiments where we got no homology between the two genome. In order to construct the physical gene map of the phage MB78, successful attempt have been made to clone EcoRI fragments of MB78 DNA into the *E. coli* ED8654 using plasmid pBR322 as a vector. Two such clones viz, pJM8 and pJM12 were found to contain MB78 EcoRI fragments B and D, respectively. Further characterisation of these clones are in progress. These clones will be helpful in constructing the physical gene map of the MB78 genome and to identify its genes involved in the morphogenesis of this phage.

Section V

Lysozyme is one of the well studied phage induced enzyme which is responsible for the lysis of the host and the liberation of phage progeny. So it was of our interest to study the properties of MB78 and P22 induced lysozymes. Both the enzymes were purified to homogeneity as shown by

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SDS—polyacrylamide gel electrophoresis under neutral condition and polyacrylamide gel electrophoresis under acidic condition. Both the proteins can be eluted from the same column of amberlite at different salt concentration. This shows that they are distinctly different proteins. The molecular weight is in the range of 20-22x10^3 daltons. The optimum pH for the enzyme activity is 7.0 and 7.4 for MB78 and P22 respectively. MB78 lysozyme activity is not inhibited upto 60 mM tris concentration, while P22 looses 60% of its activity at this concentration. Both the enzymes are active on Gram negative and Gram positive cells but the Gram negative cells acts as a better substrate. Monovalent and divalent cations are inhibitory to their activity but low concentration of $MgSO_4$ enhances MB78 lysozyme activity to an appreciable extent. Another interesting feature of MB78 lysozyme is that it is highly thermolabile i. e. looses more than 50% of its activity when heated at 40°C for min while P22 is fairly stable at this temperature. All the above charateristics shows that MB78 lysozyme resembles more closely the lysozyme induced by P22, T4 while it differs from λ which is an endolysin.

Section VI

The results presented in the Sections III-V have been considered, together to discuss in a general way the implications of the investigations presented in this dissertation.

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PEDIATRICS

NUTRITIONAL ASSESSMENT IN PREGNANT AND LACTATING WOMEN

Raj Rajeshwari Devi Sup. *Dr. K. N. Agrawal*

The influence of maternal nutritional status and stature in modifying the outcome of pregnancy as well as growth of the infant in earlier months of life created sufficient interest to plan the present study.

The objectives of the present study were to assess the nutritional status of the rural women (in both non-lactating and lactating) with special reference to the weight gain pattern during pregnancy. The effect of low nutritional status on the outcome of pregnancy was also studied. The culture of vaginal swab and urine was done to study the effect of prevalent genito-urinary infections on the anthropometric nutritional status of these rural women. The enzyme salivary protein were estimated with the hope that those could help in assessing nutritional status in these women or any other deviations during pregnancy, lactation or other hormonal events such as menstruation.

The study was conducted in 5 different villages of Kashi Vidyapith Block having a total population of 7335, out of which 1528 women were in childbearing age (15-45 yr) and eligible for pregnancy. Six hundred seventy five (44.2% of the total women in childbearing age) women were available and readily agreed to participate in the study. Out of these 675, 301 women were nonpregnant nonlactating, 267 were lactating and 107 were from both the above groups but having vaginal discharge. These women were followed every two monthly for anthropometry (weight and midarm circumference) and general health check up in a pretested and predesigned proforma (200 of the lactating and 198 of the nonlactating were followed at four different periods of the year till last, excluding the 170 women who got conceived). Those women who got conceived (from the lactating as well as nonlactating group—170 in number) were registered for further follow up during the antenatal period and immediately after delivery to study the weight gain pattern and midarm circumference change during pregnancy. Only 63 of these pregnant women could be followed till delivery (due to their migration to parent's house). The athropometry of the newborns was recorded within 48 hours of delivery to observe the effect of maternal anthropometric nutritional status on that of newborn. One hundred seven women

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having vaginal discharge were studied for the microbiological profile of their vaginal discharge and urine by subjecting their vaginal swab and urine for culture. The hemoglobin, packed cell volume (PCV), serum protein and albumin of these women were estimated. The effect of infection on the anthropometric as well as blood biochemical nutritional parameters were observed. The immunoglobulin IgG, IgM and IgA titres in the sera of these women were also estimated as an evidence of infections.

For salivary protein and salivary arginase activity, 39 pregnant, 27 lactating and 29 nonpregnant nonlactating rural women from the selected subjects were examined. In addition, salivary protein and arginase activity in 40 women in different phases of menstruation and 10 urban nonpregnant nonlactating women was also studied.

The anthropometry of mothers and the newborns was done by standard techniques. The hemoglobin was estimated by cyanmethemoglobin method, PCV was determined by microhematocrit apparatus, total plasma protein and albumin were determined by biuret method, genitourinary infections were confirmed by standard techniques employed for the culture of vaginal swab collected from the posterior fornix of the vagina, culture of midstream sample of urine and by estimating immunoglobulin titres (IgG, IgM and IgA) in the sera of these women suspicious of having infection by the radial immunodiffusion technique as described by Mancini et al. (1965), salivary arginase was estimated by the method described by Gopalkrishna and Nagrajan (1978) and salivary protein was determined by the method described by Lowry et al. (1951).

The present study revealed that most of the rural women in this part of the country were underweight (80-85% less than 45.0 kg). Mostly they were short statured (61.5 to 62.1% under 150.0 cm and 28.5 to 31.3% under 145.0 cm in height). The follow up during four different periods in the year demonstrated that the lactating mothers showed a non-significant decrease in weight, midarm circumference and triceps skinfold thickness values during first twelve months of lactation, although the nonlactating women did not show any gross fluctuation in these anthropometric parameters. These rural women show a poor gain in weight (7.0 ± 2.1 kg) during pregnancy. The gain during pregnancy was significantly related ($P<0.001$) to the period of gestation in weeks from 13th week onwards (uptil 13th week, the effect was not seen). The rate of gain during 13th to 41st week of gestation was 0.23 kg/week. The midarm circumference was also increased during 13th to 40th week. It was also significantly related to period of gestation in weeks ($P<0.005$). The women gaining more during pregnancy gave birth to healthier and heavier babies. The birth

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weight of the newborn was significantly related to the gain during pregnancy ($p<0.005$). There was a significant difference in mean birth weight in the two groups gaining ≤ 5.0 kg and more than 9.0 kg ($p<0.05$). These rural women gave birth to smaller babies (mean birth weight 2490 $\pm$ 255 g). The short statured women (<145.0 cm in height) gave birth to smaller and lighter babies than those by taller mothers (>150.0 cm in height). The mean birth weight in the above two groups differed significantly ($p<0.01$).

Further, the midarm circumference of the newborn was significantly related to that of the mother with a positive correlation ($p<0.005$). There was a significant difference in mean birth weight ($p<0.05$) in the two groups of pregnant women, one group maintaining diastolic blood pressure of <60 mm of Hg and the other group maintaining the same as 60 to 90 mm of Hg during the third trimester of pregnancy (difference in mean birth weight was 163 g). The vaginal swab culture demonstrated prevalence of Staphylococcal organisms (41.4%) of the total culture group. The culture positive group did not show any gross deviation in the anthropometric nutritional status from those of culture negative group. However, there was nonsignificant decrease of weight, midarm circumference and triceps skinfold thickness in the cases showing positive urine culture. The positive urine culture group of women also were anemic, the mean hemoglobin value differing significantly when compared to that in negative urine culture group ($p<0.05$). Further the IgG, IgM and IgA titres were increased in the sera of those women showing positive urine culture. The change in IgG and IgM were statistically significant ($p<0.01$ in each). The salivary arginase activity was distinctly lowered during all the three trimesters of pregnancy, lactation, menstruation and ovulation (12-14 days before onset of next menstrual cycle, hence presumed to be ovulating). The statistical level of significance 'p' was <0.001 in all the above groups.

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PHARMACOLOGY

EFFECT OF VEGETABLE BANANA ON GASTRIC SECRETION AND ULCERATION

Raj Kumar Goel Sup. *Dr. A. K. Sanyal*

The main aim of the present study was to assess the antiulcerogenic property of vegetable green banana powder against different experimental models of gastric and duodenal ulcers and also to determine the possible mechanism of its antiulcerogenic effect. This effort was considered worthwhile in spite of large number of therapeutic options available to the clinicians to treat peptic ulcer. The presently available drugs, however, tend to primarily act on one side of the equation which govern the treatment of peptic ulcer, namely, on the aggressive acid-pepsin factor. Only carbenoxolone can be considered to act on the other side of the equation i.e., strengthening the mucous barrier or resistance, Recent reports emanating from different laboratories including ours, indicate that 25 to 75% of duodenal ulcer cases have acid secretory range within normal limits. It, therefore, appears that more logical target of medical attack would be to find out more and more drugs which would strengthen the mucosal barrier rather than merely decrease or neutralise the acid-pepsin factor.

The choice of green vegetable banana was made because of earlier observation of antiulcerogenic property of its powder on phenylbutazone (Sanyal *et al.*, 1964) and immobilisation stress-induced (Sanyal *et al.*, 1965) ulcers in guinea pigs and rats respectively. The antiulcerogenic effect of banana was later confirmed by Elliott and Heward (1976) on histamine-induced ulcers in mice. Further, mention of high banana diet in ulcer patients has also been made in Indian and Western texts (Nadkarni, 1954; Bendlage, 1932; Hanszen, 1934; Killian, 1939). Sanyal and his coworkers however, selected green vegetable banana for its high 5-HT content (Sinha *et al.*, 1961). 5-HT had earlier been shown not only to inhibit acid secretion but also to promote mucous secretion (Wilson, 1957; Smith, 1957). The results of the present study indicate that the original premise of Sanyal and his coworkers might not be correct but that their suggestion that antiulcetogenic effect of banana might not be due to its anti-acid or any demulcent action has proved to be correct.

To study the antiulcerogenic effect of green vegetable banana, the fruits of different sizes were collected in and around Varanasi throughout

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the year and also from different parts of the country in those months when the local variety showed activity. The effect of three variables i.e., the season, soil and the size of the fruit on the antiulcerogenic property of banana powder was thus studied. The results show that the antiulcerogenic property was present in banana of bigger size (average weight 75 g) and in the months between September to March of the year. The results with banana collected from different parts of the country indicate that antiulcerogenic effect is present in banana from the northern belt of India (earlier studies of Sanyal and his coworkers were with banana collected in and around Agra) as the banana of South India did not show any antiulcerogenic activity, at least during the months of its collection for the present study.

The antiulcerogenic effect has been studied against pylorus-ligated, aspirin, phenylbutazone, indomethacin, prednisolone and immobilisation stress-induced gastric ulcers in IVRI strain of albino rats of either sex and histamine-induced gastric and duodenal ulcers in locally procured male guinea pigs. The green vegetable banana powder (DRBP) has been found to protect the animals from the ulcerogenic effect of all except histamine-induced gastric ulcers in guinea pigs. The available data can not explain the failure of DRBP in histamine induced gastric ulcer but one may feel prompted to make a naive suggestion that histamine-induced gastric ulcers being H_1- mediated responses, are not likely to respond to antiulcerogenic drugs which act primarily on different parameters of gastric secretion. DRBP has been found to have no *per se* significant effect on acid-pepsin secretion but has been found to have actions on factors which are said to augment the mucosal resistance.

Of the factors which govern mucosal resistance, namely, (i) mucosal blood flow; (ii) integrity of the mucosal barrier to back diffusion of H^+ ions; (iii) secretion of mucous; (iv) regeneration of epithelial cells and (v) local synthesis of prostaglandins, DRBP has been found to affect secretion of dissolved mucosubstances in terms of its carbohydrate : protein ratio and to strengthen the functional integrity of mucosa (to resist the back diffusion of H^+ ions) by quicker cellular proliferation resulting in increased mucosal thickness and increased sialomucin content in the epithelial cells, No effort has been made to study the effect of DRBP on mucosal blood flow. Some preliminary results of a colleague, Dr. S. B. Acharya, indicate that DRBP caused a very significant increase in the secretion of prostacyclins. Prostacyclins have been reported to possess all the actions of 'classical' prostaglandins i.e., of PGE_2, which is endowed with its well established cytoprotective character. If this latter observation on the effect of DRBP to promote secretion of prostacyclins, is confirmed in subsequent

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studies in this laboratory, four of the five of criteria governing the mucosal resistance would be fulfilled by DRBP. Thus, DRBP may be said to act by strengthening the mucosal resistance,

In the present study, dissolved mucosubstances in the gastric juice have been studied in 95% alcoholic precipitate instead of the usual lyophilised-nondialysable fraction. A recent comparative study of these two methods showed that similar qualitative information could be obtained by these two methods (Sanyal *et al.*, 1983). DRBP and deglycyrrhizinated liquorice (DGL) showed a *per se* increase in the carbohydrate : protein ratio of the dissolved mucosubstances and all the ulcerogenic agents used namely aspirin, indomethacin, phenylbutazone and prednisolone significantly decreased it. DRBP treatment has been observed to reverse the ulcerogenic drug-induced decrease in carbohydrate : protein ratio.

Alcian blue staining of the sections of the stomach showed more intense staining in DRBP treated animals compared to controls, indicating an increase in the sialomucin. Aspirin significantly decreased it and DRBP reversed the aspirin induced decrease.

DRBP and DGL caused a significant thickening of gastric mucosa of the rat stomach. Aspirin did not have any *per se* effect. This increase in the mucosal thickness is probably due to increased cellular proliferation as evidenced by increase in the *in vitro* thymidine-H^3 uptake by the gastric mucosal cells and by Feulgen stain method for DNA.

Any drug causing increase in the cellular proliferation must be looked into suspiciously for any teratogenic effect. An attempt has therefore, been made to find out any morphological deformity or any other obvious changes which could be attributed to the teratogenic effect in rats kept on banana (chips) supplemented diet for three generations. The offsprings of all the three generations did not show any apparent deformity and their growth pattern was normal compared to controls. 70 day old 3rd generation rats were also employed to study the chronic systemic effect, if any, of DRBP. Nothing abnormal (liver, kidney or haemotological) could be detected compared to controls.

Treatment with DRBP for varying period was found to cause a significant increase in gastric mucosal 5-TH content; 3 day treatment caused a significant increase compared to controls; 30 day treatment caused for further significant increase compared to 3 day treatment; 70 day old 3rd generation rats, however, did not show any further increase in the gastric mucosal 5-HT content compared to 30 day treatment with banana. Brain 5-HT was also estimated in the 3rd generation rats which showed no significant increase in the 5-HT content compared to control.

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The increase in the gastric mucosal 5-HT content cannot, however, be related to increase in mucous secretion or to augment the mucosal resistance factors because DGL treated rats did not show any *per se* increase in 5-HT though mucosal thickness, increase in the thymidine-H^3 uptake and also an increase carbohydrate: protein ratio of the precipitated gastric juice.

An attempt was made to find out if possible, the active antiulcerogenic principle of DRBP. The effort however, has not met with the desired success though cold benzene and methanol extracts showed significant antiulcerogenic activity against aspirin-induced ulcers. The dose of cold benzene and metnanol extracts were 60 and 40 times less respectively than DRBP which was 0.5 g/Kg BD. Water extract also showed antiulcerogenic activity but this was less than cold benzene and methanol extracts. Methanol extract (12.5 mg/Kg BD x3 days) also significantly protected the pylorus-ligated ulcer in rats and histamine-induced duodenal ulcer in guinea pigs.

The whole exercise of studying the antiulcerogenic activity of DRBP and its possible mechanism of its action would have been merely academic if its clinical potentiality was not assessed. An uncontrolled pilot clinical trials was, therefore, undertaken to see the clinical efficacy of banana powder (i g, QID) in patients of ulcer and nonulcer dyspepsias. Sixteen of the 19 patients who completed the course of 3 months showed complete clinical recovery though radiologically only 7 out of the 12 patients showed improvement. Encouraged by these results, banana powder was administered to endoscopically proved duodenal ulcer patients. These patients however, did not show either the expected clinical or endoscopic improvements. In retrospect, the reason for this failure could be ascribed to the time of collection of banana viz. from the months of June to October. After studying the seasonal variation, enough quantity of the active banana powder (DRBP) has been collected for a more systematic control randomised study to determine its antiulcerogenic efficacy. At the moment 2 endoscopically proved duodenal ulcer patients are on DRBP, supplied to them in capsules. Both these patients, have not only shown a marked symptomatic relief but one has shown the sign of healing after endoscopic examination at six weeks of starting DRBP. Symptomatic relief is usually observed within 3 to 7 days after the start of the treatment. This further substantiates the experimental observation that DRBP does not act like anti-acid, and its antiulcerogenic activity may not be due to demulcent action (Sanyal *et al.*, 1964). Few patients who were earlier treated with banana powder have maintained their contact and can be said to have no recurrence within 4 years since stoppage of the treatment.

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The result of the present study helps us to draw the following conclusions :

1. Green vegetable banana powder affords significant protection against aspirin, indomethacin, phenylbutazone, prednisolone, immobilisation stress-induced gastric ulcers in rats and histamine-induced duodenal ulcers in guinea pigs.
2. The antiulcerogenic effect of banana powder is not due to any anti-acid or anti-pepsin activity.
3. Banana powder affords protection against different models of experimental ulcers by augmenting the mucosal resistance as evidenced by (i) its effect on the character of dissolved mucosubstances (in terms of carbohydrate : protein ratio), (ii) thickening of the gastric mucosa by increased cellular proliferation (Thymidine-H^3 uptake study and Feulgen stain for the DNA), (iii) increased sialomucin content of the gastric mucosa (alcian blue stain), (iv) a possible induction of synthesis of prostacyclins.

   Thus DRBP seems to fulfil 4 of the 5 accepted criteria which determine the mucosal resistance.
4. Though banana powder do cause cellular proliferation, it does not seem to posses any teratogenic effect as evidenced by follow up studies of rats kept on banana supplemented diet for three generations.
5. Prolonged treatment with banana powder does not produce any systemic toxic effects.
6. The antiulcerogenic activity of banana seems to vary with season, soil and size of the fruit.
7. Antiulcerogenic activity of banana is present in benzene and methanol extracts. The aqueous extract also possesses antiulcerogenic activity but it is much less compared to benzene or methanol extracts.
8. Banana appears to have clinical potentiality for the treatment of ulcer and non-ulcer dyspepsias.

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STUDIES ON THE POLAROGRAPHIC METHODS OF ANALYSIS OF DRUGS

Arvind Kumar Mishra Sup. *Dr. K. D. Gode*

Polarography, as the term coined by Heyrovsky (1922) to designate the determination of current-voltage curves with the dropping mercury electrode (d.m.e.), as an indicator electrode, was the first of the voltametric techniques to gain prominence and is still the most widely used method because of the several advantages peculiar to the d m.e, in the analysis of biochemical, pharmaceutical, toxicological, industrial and clinical nature of the substance. It can be used directly for the determination of any substance (Meites, 1965)—solid, liquid or gaseous, organic and inorganic—ionic or molecular—that can be dissolved in a solvent of reasonable dielectric constant and either reduced or oxidized at a mercury electrode. This includes the ions of nearly all metals and many non-metals and also organic compounds with polarographically active functional groups such as conjugated double or triple bonds including polynuclear ring systems, as well as compounds like nitro, nitroso, azo, hydroxylamino, oximes, imines, ketones, aldehyde, azomethine, peroxy, disulfide and halo-substituted compounds. In addition to this, organic compounds having no such functional group can also be made quantitatively estimable by means of some indirect methods.

Furthermore, polarography has been demonstrated to be an excellent analytical method (Brooks and De Silva, 1975) for the quantitative estimation of drugs in their pharmaceutical dosage forms such as tablets, combination tablets, capsules, syrups, powder, injection, mixture, cream, soluble ointments etc., as well as in biological materials such as blood, serum and urine samples. They have pointed out that polarographic analysis is of great utility because in some cases it shows greater sensitivity than spectrophotometric methods and comparable sensitivity to most spectrophoto-fluorimetric methods and gas-chromatographic assays based on the use of flame-ionization detectors.

With this perspective, the present investigation has been attempted to study the polarographic behaviour of some of the important drugs, and to estimate them in their pharmaceutical dosage forms.

Drugs generally contain organic compounds and these organic compounds have some functional group(s) which can be easily reduced or oxidized at d. m. e. and estimated directly. These functional groups are classified as polarographically active functional groups and include $>C=C<$, when conjugated with another double or triple bonds, an

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aromatic ring or another unsaturated group; >C=O group in aldehydes, ketones and quinones; $-NO_2$, -NO, >C=N-, amine oxide and -N=N-; phenylhydroxylammonium, diazonium and quarternary ammonium groups, most of the halogens, disulfides, peroxides and epoxides etc. (Willard *et al.*, 1965). Some times, drugs lacking the above functional groups can also be made polarographically estimable by the use of some indirect methods (Meites, 1965).

For the present study, only those drugs except trifluoperazine hydrochloride, were taken for the direct polarographic analysis which has atleast one polarographically active functional group. The selected drugs are—nitrazepam nitroxazepine hydrochloride, nialamide, nitrofurazone, furazolidone and niclosamide. Trifluoperazine hydrochloride has no functional group that can be reduced at d. m. e. and therefore, its estimation in tablets was carried out by an indirect method involving complex formation with silicotungstic acid which gave a well-defined reduction wave at d. m. e.

Five different buffer syetems with acidic to alkaline pH range were selected which served as supporting electrolytes because the use of supporting e'ectrolyte in the polarographic analysis is must. For the quantitative estimation of the drugs in their pharmaceutical dosage forms standard addition (Hohn, 1937) method was used.

A general polarograph 's' in conjunction with the spot galvanometer was used. The current-voltage measurements were performed at a dropping mercury electrode (d. m. e.) versus a saturated calomel electrode (S. C. E.) used as a reference electrode. The potential applied was from 0.0 to 2.0 V.

For all polarographic measurements, Triton X-100, which is a polyethylene glycol ether of monoiso-octylphenol was used as maximum suppressor. 0.1 ml of the stock solution (0.2 per cent) was sufficient in each 10 ml of the solution to be analyzed. The dissolved oxygen removal from the polarographic solution was performed by passing a continuous stream of oxygen-free nitrogen for 10 to 15 minutes, depending upon the nature of polarographic testsolution. The removal of dissolved oxygen was necessary because the oxygen gets itself reduced at the dropping mercury electrode.

General Polarographic Behaviour

All the polarographic measurements were performed at $25 \pm 0.2^{\circ}C$. In general, the drop time was maintained at 2.96 second with an open circuit and the product $m^{2/3} t^{1/6}$ was 1.98 $mg^{2/3} sec^{-1/2}$ at a mercury column height (h) of 60 cm. The general polarograms of the drugs were recorded in the concentration range 1.0×10^{-4} to 7.5×10^{-4} M. For studying the polarographic behaviour of the drug, the effect of various

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parameters such as increasing drug concentrations, temperature, pH, mercury column heights, mixed-solvent composition was taken into account. The effect of pharmaceutical adjuvants commonly employed in the formulation of the drug dosage forms was also evaluated by taking the polarograms of the synthetic mixtures of various adjuvants and the drug under investigation.

Controlled-potential electrolysis was also carried out in order to determine the total number of electrons involved in the overall reduction process of the drug at d. m. e. in each individual buffer system. The controlled-potential electrolysis was performed in a modified Lingane H-type cell.

Analysis of Pharmaceutical Dosage Forms

Two methods both involving 'standard addition' were employed for the quantitative estimation of the drugs in their pharmaceutical dosage forms. In one case, a calibration graph was prepared with pure drug and comparison was made with the dosage content. Whereas, in the other case milligrams of the drug content per tablet/capsule was determined utilizing an empirical formula as suggested by Marjan (1976).

The quantitative estimation of each drug was performed according to the known official methods and the results obtained were compared with that of polarographic data.

Trifluoperazine hydrochloride which has no polarographic active functional group that can be reduced at d. m, e., and therefore, its esimation in tablets was performed, by an indirect method in which a complex was formed with silicotungstic acid in strongly acid solution.

Nitrazepam has two polarographic active functional group that can be reduced polarographically. Nitrazepam gave two step reduction wave in all the buffer system taken over their entire pH range. Well-defined waves were observed in each of these buffer system over a certain pH range. The nature of both the nitrazepam waves was found to be diffusion-controlled in each of the buffer systems taken. Their diffusion currents were linearly dependent on square-root of column height. The half-wave potentials of nitrazepam wave were -0.25 and -0.86 V in the hydrochloride buffer at pH 2.00. Half-wave potentials in the similar range were also observed in other buffer systems.

The comparison of the polarographic method with that of spectrophotometric method shows that the proposed polarographic method is equally sensitive to spectrophotometric method and the results obtained

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by both the methods are in close agreement. Therefore, the polarographic method can safely be used as an alternative to the specified official spectrophotometric method.

Nitroxazepine hydrochloride has a nitro group at position-2-and at d, m. e. it gets reduced to corresponding hydroxylamine derivative. It gave single four-electron reduction wave in all the buffer taken over their entire pH range. In hydrochloride buffer (pH 1.00—2.20) the reduction of the nitro group started at the very start of the potential. Therefore, for quantitative estimation purposes this buffer was not chosen.

The reduction wave of nitroxazepine hydrochloride was found to be irreversible and diffusion-controlled. The half wave potential was found to be dependent of pH and shifted towards more negative potentials. For acetate (pH 3.60 to 5.60) McIlvaine's (pH 2.20 to 8.00), Britton-Robinson's (pH 2.00 to 12.00) and borate (pH 7.80 to 10.00) buffers the slope value of the $E_1/_2$ versus pH plot was found in the range 0.055 to 0.089. With the proposed polarographic method, nitroxazepine hydrochloride can be estimated upto the limit of 0.37 µg per ml.

A spectrophotometric assay method has also been proposed for the estimation of nitroxazepine hydrochloride in both the tablet dosage form available by measuring the absorbance at about 270 nm and the results are compared with that of polarographic method. The comparison of the polarographic results with that of spectrophotometric method are in close agreement. These results along with that of recovery experiments advocate the accuracy and reproducibility of both polarographic as well as spectrophotometric methods.

Nialamide gave a well-defined single reduction wave in the buffer systems taken. The nature of the wave was found to be irreversible and diffusion-controlled. The polarographic method developed was found suitable for the estimation of nialamide tablets. In the pure form, nialamide can be estimated upto the concentration as well as 2 – 5 µg per ml. None of the excipients commonly employed in the formulation of drug dosage form was found to interfere with the assay of the drug.

Nitrofurazone gave two polarographic reduction wave in the acetate (pH. 3.60 to 5.60), McIlvaine's (pH 2.20 to 8.00), Britton-Robinson's (pH 2.00 to 12.00) and borate (pH 7.80 to 10.00) buffers over the entire pH range. The nature of both the waves was found to be diffusion-controlled and irreversible.

The polarographic method has been attempted to estimate nitrofurazone in available dosage forms.

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The polarographic methods have further extended to study the polarographic behaviour of few other drugs such as furazolidone and niclosamide.

Both the drugs have polarographically active functional groups that can be reduced at the d.m.e.

Trifluoperazine hydrochloride, a member of phenothiazine group, has no functional group that can be reduced at the dropping mercury electrode. To estimate the drug, an indirect polarographic method has been proposed which involves the complex-formation with silicotungstic acid in concentrated hydrochloric acid solution. Silicotungstic acid is known to give well defined wave in the hydrochloric acid. By measuring the decrease in the diffusion current, the amount of the drug has been calculated.

Thus, polarographic methods have been developed for the aforesaid seven drugs and the results obtained were found to be in good correlation with that of the official assay methods. This may provide another suitable analytical technique for the routine analysis of the above drugs.

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PSYCHIATRY

AN INVESTIGATION INTO PLANNED THERAPEUTIC GENERALIZATION OF TREATMENT—EFFECTS IN STAMMERING/ STUTTURING

Sarada Devi Sup. *Dr. Ratan Singh*

The referred patient, after screening for psychosis and mental retardation, and florid psychoneuretic symptoms, was taken into clinical intake work. The clinical intake involved case-history taking, administration of questionnaires including the stuttering severity scale, self-ratings of stammerer, heart rate recording in the context of imagined situations triggering stuttering. The subjects then entered the Stage 1 which was the setting-stage for Stage 2. Stage 1 involved various treatment procedures e. g., metronome procedure, slowed speech procedure and their various combinations, and series of evaluation sessions.

Stage 1 set the stage for stage 2 which is the present work. Subjects who, as a result of Stage 1 procedures had achieved improvement in the clinic but continued to stutter in their natural life setting were the subjects of Stage 2. Such subjects were 10 in number.

Stage 2 : The experimental design used in the present work, was the one suitable for clinical research namely, the non-concurrent multiple-baseline design across-subjects.

Generalization baseline evaluation sessions made the beginning of the Stage 2. The time length of generalization baseline evaluation sessions did depend on the specific baseline time lag to which the subject was alloted as befitting the general formate of multiple baseline design. The generalization baseline evaluation sessions differed from the evaluation sessions of stage 1 in two respects : self-ratings by stammerers of their stammering in the natural life setting were part of the stage 2 evaluation sessions, and stranger was present during the stage 2 evaluation sessions involving in--clinic tape recordings of subject's speech.

If the subject was not found to achieve generalization criteria, during the generalization baseline evaluation sessions, then he was put on generalization phase 1 namely, self-control via self-monitoring (S. M. Phase). In this phase the subject was asked to note down the occurrence or nonoccurrence of stammering each half hour daily for 7 days in his

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daily life settings. Thereafter were followed the series of evaluation sessions. If the subjects were found not to achieve generalization criteria by this time, then they were put in the systematic desensitization phase (S. D. Phase). The S. D. Phase was according to the standard procedure of systematic desensitization enunciated by Joseph Wolpe (1958). After the desensitization was complete on the hierarchy of stimulus situations there aga in followed the series of evaluation sessions. If the subject was still found not to achieve the generalization criteria, he was taken into the next generalization procedure namely, assertion training phase, there were only two cases who had to come upto this phase. These two subjects however dropped out in the middle of their assertiveness training programme.

Except for the drop-outs, all the cases having achieved generalization criteria were administered questionnaires before and after the series of generalization porcedures of stage 2 and were then put on follow-up. The follow-up consisted of the usual evalutation sessions and communication through postal letters.

Evaluation Sessions :

When—the evaluation sessions were conducted at the end of each treatment procedure phase of stage 1 and each generalization procedure phase of stage 2 and also in the generalization baseline phase and follow-ups.

Kinds—There were four kinds of evaluation sessions :

1. Tape recorded evaluation sessions, consisted of spontaneous speech and reading by the subject in the clinic in the presence/ absence of stranger.
2. Polygraphic recording of heart rate in the laboratory while the subject imagined some stutter-triggering scene.
3. The administration of stuttering severity scale in the clinic.
4. Ratings in daily life settings.

Clinic Criteria : were defined as; not more than one 10—seconds' dysfluent interval in any five-minutes trial, out of three 5-minute trials of spontaneous speech, and not more than three dysfluent words in any 300—word trial block through five trial blocks. Additionally, these criteria were to be maintained for three successive evaluation sessions through three days in sequence.

Generalization Criteria : Same as the clinic criteria with the difference that now the criteria were to be achieved in thep resence of a stranger

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and the subjects' *invive* self-ratings of stuttering in their natural life settings were also obtained and they were to be "mild" or "practically not at all", and also maintained as such for five days.

Inter-observer reliability :

The ratings of subject's stuttering were collected from him and also from his family member or close companion for estimating reliability. Regarding the tape recorded material, it was analyzed by two observers. In the spontaneous speech condition the agreements (about presence/absence of stammering) between the two observers were counted interval by interval through each 10-seconds interval and the reliability was calculated by the usual formula for percentage of agreement. In reading condition, the percent agreement about fluent words as observed by the two observers in a 300—word passage was calculated.

Results :

Results have been presented graphically, in non statistical format, for each individual subject, following the model of multiple beseline designs. Four subjects had achieved the generalization criteria in generalization baseline phase, and 10 subjects had entered the Stage 2, out of whom, four had reached the criteria in S. M. Phase, three went upto S. D. Phase, and three dropped-out in the midst of the study, one in S. D. Phase and two in Assertive training phase.

Systematic follow-up of six months has been reported on most of the cases and follow-up of 18 months has been reported on some cases.

The main content was that subjects who do not generalize with treatment effects can be specifically helped to achieve generalization by means of self monitoring or systematic decensitization. The unique role of the two techniques is discussed.

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FACULTY OF SCIENCE

BIOCHEMISTRY

STUDIES ON THE MOLECULAR SYMMETRY RELATED PROPERTIES OF PLANT GLYCERALDEHYDE 3-PHOSPHATE DEHYDROGENASE

Srinivasan Sup. *Dr. O. P. Malhotra*

Properties of two plant glyceraldehyde 3-phosphate dehydrogenases (GPDHs) (each a tetrameric molecule of apparently, identical monomers) related to the site-site heterogeneity and half-site reactivity, have been investigated. The results are summarized below :

(1) Thermal inactivation kinetics of purified GPDH from germinating mung beans (*Phaseolus aureus*) have been investigated under different conditions of temperature and pH in the absence and presence of substrate and coenzyme ligands. The apo-enzyme solution loses activity in two distinct phases, and the kinetics can be described by a sum of two first-order terms, Eq. (1).

$$A_t = A_{fast}.e^{-k_{fast}.t} + A_{slow}.e^{-k_{slow}.t} \quad \ldots\ (1)$$

where A_t is residual activity at time t, A_{fast}, A_{slow}, k_{fast} and k_{slow} are amplitudes and rate constants of the fast and slow phases, respectively. Sum of A_{fast} and A_{slow} is equal to the initial activity. At lower pH (7.3 or less), $A_{fast} = A_{slow} = 50\%$ of the initial activity. With increasing pH values the percent contribution of the fast phase ($\%A_{fast}$) increases with a corresponding decrease in $\%A_{slow}$. At pH 8.5, and above the loss in activity is described by a single exponential term ($A_{solw} = O$ and $A_{fast} = 100\%$) with a first-order rate constant equal to k_{fast} observed at lower pH values. These observations suggest that the enzyme tetramer exists in two conformations of different symmetry characteristics. The conformation in which the tetramer exhibits pair-wise arrangement of subunits towards thermal stability (C_2 - state) predominates at pH 7.3 and below, while the other conformation in which all the sites are equivalent in thermal stability (D_2 – state) predominates at pH 8.5 and above. The two conformations are freely interconvertible and the interconversion is very fast. This is shown by experiments in which the enzyme was subject-

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ed to a "sudden pH change" and then to thermal inactivation. The kinetic pattern was characteristic of the final pH at which the enzyme was heated.

C_2 - symmetry conformation $\rightleftarrows$ D_2 - symmetry conformation

Since D_2 - symmetry conformation predominates at higher pH, its formation from the C_2 - symmetry conformation must be accompanied by loss of protons. A plot of $\%A_{fast}$ against pH gives a typical sigmoid curve with midpoint at about pH 7.9. Stoichiometry of proton loss could not be established, but the data suggest that it should be greater than one. Uptake of protons by D_2 - symmetry conformation to form C_2 - symmetry conformation exhibits a weak positive cooperativity (slope of Hill plot = 1.3). Temperature (35 to 52°) does not affect the kinetic pattern (biphasic or single exponential decay). It affects the rate constants, only.

(2) Since the kinetics of thermal inactivation show different palterns at pH 7.3 and 8.6. the effect of ligands have been studied at both these pHs. At pH 7.3 (47°), NAD^+ (0.63 mM) does not affect the kinetic pattern which remains biphasic with $A_{fast} = A_{slow} = 50\%$ of initial enzyme activity. The two rate constants (k_{fast} and k_{slow}) decrease in the presence of NAD^+, *albeit* to different extent. At higher pH(5 5,60°). NAD^+ brings about a change in the kinetic pattern from a single first-order decay (in the apo-enzyme) to biphasic with $A_{fast} = A_{slow} = 50\%$ of initial enzyme activity. The data suggest that NAD^+ binds preferentially to the C_2 - symmetry conformation of the enzyme.

(3) The substrate, glyceraldehyde 3-phosphate (G - 3 P), offers a weak protection to enzyme at pH8.6 (30°) without affecting the kinetic pattern of loss of the enzyme activity, which remains single exponential decay. At the lower pH (47, 52°), however, (G - 3 - P alters the kinetic pattern, without affecting the two first-order rate constants. The amplitude of the slow phase (A_{slow}) increases gradually (with corresponding decrease in A_{fast}) on increasing G - 3 - P concentration. At about 50 uM G - 3 - P, the entire enzyme activity is destroyed in a single exponential decay with a rate constant equal to k_{slow} of thermal inactivation of apo-enzyme. The data suggest a very tight (almost stoichiometric) binding of G - 3 - P to the enzyme. Further, G - 3 - P must bind preferentially to the D_2 - symmetry conformation. Note that at pH 7.3, G - 3 - P "appears to" induce symmetry in an asymmetric tetramer. The stoichiometry of G - 3 - P binding has been determined at pH 7.3 at 0 - 4°, using ultrafiltration membrane cones. 4.1 moles of G - 3 - P are bound per mole enzyme (i.e. one G - 3 - P molecule per subunit) in a non-cooperative manner.

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(4) At still higher G-3-P concentrations (>80 μM) the inactivation of the enzyme follows a single exponential decay (with the rate constant close to k_{slow} of inactivation of apo-enzyme), but it is preceded by a lag period. The lag period is a function of G-3-P concentration taken. Considering the half-life of G-3-P (determined separately), under the conditions of the experiment. it could be shown that G-3-P concentration after the lag period was always in the range of 90-100 μM. The data suggest that some additional substrate molecules (beyond 4 mentioned in the preceding paragraph) are bound to the enzyme at high G-3-P concentrations (80-100 μM) at higher temperature, which render the enzyme stable towards thermal inactivation.

(5) The kinetics of thermal inactivation of GPDH in extracts of mung beans vary from biphasic in the extracts of ungerminated seeds to a single exponential decay with the extracts of seeds germinated for 36 hrs. The changing pattern of thermal inactivation of GPDH in the crude extract of seeds has been correlated to the changing level of G-3-P during germination. The substrate also protects the enzyme against proteolysis.

(6) Mung bean GPDH contains 3.9 very reactive SH groups per mole tetramer (i. e. one SH group per subunit). Two of these SH groups react with excess 5,5' -dithiobis (2-nitrobenzoate) (DTNB) faster than the other two at pH 7.3 (Eq. (2)).

$$\triangle A_t = \Delta A_{co} - \frac{\triangle A_{co}}{2} \left(e^{-k_{fast} \cdot t} + e^{-k_{slow} \cdot t} \right) \quad \text{.... (2)}$$

where $\triangle A_t$ is the corrected absorbance increase at time t and $\triangle A_{co}$ the corrected value of absorbance increase when all the reactive SH groups have reacted with DTNB. k_{fast} and k_{slow} are the pseudo-first-order rate constants for the fast and slow phases, respectively. Both the rate constants show first-order dependence on DTNB concentration, but the relative distribution of the two sets of SH groups is independent of DTNB concentration. At high pH (pH 8.6) the reaction of reactive SH groups become very fast and its kinetics cannot be monitored by conventional methods.

Thus, the inherent pair-wise arrangement of subunits in apo-GPDH at pH 7.3, as suggested by the results of thermal inactivation, is also observed in the chemical reactivity of the reactive SH groups.

(7) Addition of NAD+ does not affect the kinetic pattern and k_{fast} of reaction of the enzyme with DTNB, but k_{slow} decreases. The NAD+ concentration-dependent change in k_{slow} has been utilized to study the binding of NAD+ to the enzyme. A hyperbolic (non-interacting sites) saturation is observed, with Kdissociation equal to 105 uM.

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(8) G-3-P does not affect the kinetics (the relative amplitudes or the two rate constants) of the reaction of DTNB with mung bean GPDH. This observation rules out the formation of any hemithioacetal bond between the substrate and the essential SH groups.

(9) As with other GPDHs, the reaction of mung bean GPDH with excess G-3-P and NAD^+ (in the absence of phosphate or arsenate) results in the formation of a finite amount of NADH (Eq. (3)).

$$R-\overset{\overset{O}{\|}}{C}-H+E-SH+NAD^+ \rightleftarrows R-\overset{\overset{O}{\|}}{C}-S-+NADH+H^+ \quad \ldots(3)$$

Stoichiometry of NADH formation (and therefore, acylation of the enzyme) increases gradually from 1.8 to 3.6 moles per mole tetrameric enzyme, as the pH of the solution is increased from 7.3 to 8.6. Assuming four equivalent and non-interacting acylatable sites per molecule of GPDH (since G-3-P favours the D_2-symmetry conformation) and neglecting any enzyme-substrate complex, an apparent equilibrium constant (K'_{eq}) has been calculated at different pHs.

$$K'_{eq}=\frac{[R-\overset{\overset{O}{\|}}{C}-SE]\,[NADH]\,[H^+]}{[R-\overset{\overset{O}{\|}}{C}-H]\,[E-SH]\,[NAD^+]}=(5.6\pm1.2)\times10^{-7}$$

Effect of G – 3 – P concentration on the stoichiometry of the reaction of Eq. (3) has been studied at pH 7.3 and 8.6. At the higher pH, which favours the D_2 – symmetry conformation of the enzyme, the value of K'_{eq} is not affected by the G – 3 – P concentration (6 to 625μM). At pH 7.5, K'_{eq} is constant for G – 3 - P $>$ 23μM. However, at G – 3 – P concentration ($<$ 23 μM), at pH 7.5, where the C_2 – symmetry conformation predominates, K'_{eq} decreases to approximately 10^{-9}. It appears that in the oxidation-reduction reaction, the enzyme in the C_2 – symmetry conformation is acylated with great difficulty, if at all.

(10) GPDH from another plant source (pea seeds; *Pisum sativum*) has been purified about 200-fold. The purified enzyme shows a single protein band on polyacrylamide gel electrophoresis in the absence and presence of sodium dodecyl sulphate. The electrophoretic mobility of the enzyme protein band, in the presence of sodium dodecyl sulphate corresponds to a subunit molecular weight of 38,000. The enzyme exhibits a typical protein spectrum with maximum absorption at 278 nm and $\epsilon^{0.1\%}_{280}=1.04$. The A_{280nm}/A_{260nm} ratio is equal to 1.5 and does not change

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on further treatment of the purified enzyme with charcoal or cellulosic ion exchangers. Enzymatic estimations of bound NAD+ shows less than 0.08 mole of NAD+ per mole enzyme tetramer.

(11) On thermal inactivation, the pea enzyme loses its activity in two distinct phases consistent with Eq. (1), where $A_{fast} = A_{slow} = 50\%$ of the initial activity. The activity lost due to the fast phase is reversed in a time dependent process on cooling ('annealing') at 0°. The slow phase is irreversible, suggesting the following scheme for the thermal inactivation of pea GPDH.

$$\text{Active enzyme} \underset{\text{(cold)}}{\overset{\text{fast}}{\rightleftarrows}} \text{Half active enzyme} \xrightarrow{\text{slow}} \text{Inactive enzyme}$$

The kinetic pattern remains unaltered in the presence of AND+ and phosphate, although both the rate constants decrease considerably (to different extents).

(12) The pea seed enzyme possesses 3.8 reactive SH groups per mole (i. e. one reactive SH group per subunit) as determined by titration with DTNB. On treatment with excess iodoacetate (30 μM) or N-ethylmaleimide (20 μM), the enzyme loses its activity in a single exponential decay, However, the loss in enzyme activity on treatment with p-chloromercuri benzoate (pCMB) (0.6 μM) shows biphasic kinetics consistent with Eq. (1), where $A_{fast} = A_{slow} = 50\%$ of the initial activity. Thus, the sites of pea seed GPDH exhibit heterogeneity (and pair-wise arrangement) in stability towards heat, reversal of thermal inactivation of annealing and in the reaction with pCMB, but are equivalent in their reaction with other iodoacetate and N-ethylmaleimide.

The above data have been discussed in the light of the earlier hypotheses on half-site reactivity. It has been concluded that GPDH exists in two interconvertible conformation of different symmetry characteristics (namely of C_2 – and D_2 – symmetry). The enzyme exhibits half-site reactivity or equivalence among sites depending upon the conditions (specially pH) and the nature of ligands which may favour one or the other conformation.

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BOTANY

SOIL-PLANT-WATER RELATIONSHIP IN A SALINE (TERRESTRIAL) ECOSYSTEM

Zacharia Joseph Sup. *Dr. G. N. Chaudhari.*

The thesis embodies two sections. Section I adumbrates field study on salt-affected habitates around Varanasi in relation to climatic, vegetational and edaphic characteristics. Section II deals with the ecophysiological studies of two populations of *Eclipta alba* Hassk. occurring on contrasting habitats (non-saline and saline) in the Indo-Gangetic plains of Varanasi.

The two populations were investigated both in the field, as well as under reciprocally planted conditions. Growth behaviour of the two populations were studied in respect of biomass accumulation, RGR, LAR, NAR, per cent plant nitrogen content, foliar chlorophyll content, transpiration, photosynthesis and the levels of different free amino acids at different stages of growth of the plants with a view to substantiate the claim that such a distribution of the species over contrasting habitats throughout the vast expanse of Indo-Gangetic plains of the Indian sub-continent is due to their genecological specialization.

The sites embraced in the present investigation were characterized by low organic matter, low nitrogen, low phosphorus and excessive amount of exchangable sodium coupled with high pH and high electrical conductivity (about 4 mmhos/cm at 25 C). Vegetation was sparse and was interspersed with barren spots of salt crusts of variable dimensions.

The ecophysiological study of *Eclipta alba* from contrasting habitats revealed that populations are recognizable to represent different units attuned to local habitat conditions on a number of parameters, e. g., growth behaviour, biomass production, foliar chlorophyll content, transpirational loss of water as well as their rates, CO_2 absorption as well as their rate of utilization, water use efficiency and free amino acid contents.

The plants of saline population persistantly demonstrated, a delayed germination of seeds and early flowering besides reduction in growth, leaf number and leaf area relative to their counterparts occurring in normal habitats. Higher biomass production by plants of non-saline population in normal habitat may be considered as an additional indication of the ecological difference in the habitat. Likewise, persistantly better perfor-

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mance of saline population in saline habitat with their having a higher RGR and NAR is indicative of their successful ecesis in the nutrient deficient salt affected habitats. Comparatively lower LAR values of the saline population in saline habitat also reflects adaptation of the biotype to the adversities associated with saline and alkali habitats.

Differences in nitrogen content of the habitat is well reflected in the uptake and utilization of the element by the two populations raised under culture conditions. That incorporation of nitrogen into chlorophyll is highly reduced by salinity may be taken to the substantiated by reduced chlorophyll content in the leaves of saline population.

Lesser transpirational loss of water as well as relativity low CO_2 absorption by saline population are attributable to the reduction in leaf area which is an adaptation towards halophytism. Further, accumulation of proline and other amino acids in the free amino acid pool of the saline populations of *Eclipta alba* also indicate with certain degree of definiteness, an adaptation towards soil salinity as these are known to play a role in osmoregulatory mechanisms of the plants under saline environment. Thus, the wider distribution of the species over contrasting habitats is explainable on the basis of ecotypic differentiation embracing both morphological as well as physiological characters modified in reponse to edaphic environment. Since sodium in the edaphic environment plays a key role in triggering this differentiation of the species, it has been considered, in the fitness of things, to designate the intraspecific variant to be a "halo-ecotype".

ECOLOGICAL STUDIES OF *CARTHAMUS TINCTORIUS* LINN. FROM VARANASI

Lalit Kumar Sup. *Dr. H. R. Sant*

Ecological consideration of crops help to understand the kind and responses to the variations in stressess of environmental components. It indicate explicitly the suitability of a species for cultivation in a particular area. In agriculture economic considerations override ecological considerations. The increasing deficit of edible oils has necessiated development efforts on new crops such as sunflower, safflower and soybean. *Carthamus tinctorius* Linn. (safflower) is a potential oil seed crop of the world. It has a long history of cultivation in India and other countries. Present study deals with the ecological considerations of two cultivars, HUS-304 (spiny

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form) and CTS-7403 (spineless form) of *C. tinctorius* crop. The crop was grown in monoculture. Field observations and sampling were made at 15 days age interval over a period of 180 days.

Seeds were found non-dormant and highly viable. Germination was found to be affected by temperature, pH and moisture stress. The most suitable period for seedling emergence and establishment was found to be between September and November. Edaphic conditions seed storage period and intraspecific competition were found affecting seedling emergence and establishment.

The total plant biomass with aging followed sigmoidal curve. The total dry matter production was found to be 722.64 ± 77.50 g/m^2 (HUS-304) and 1063.20 ± 130.10 g/m^2 (CTS-7403) at final harvest, i. e., 180 days of growth period. The peak values of net primary productivity were 11.15 g/m^2/day in HUS-304 at 105 day and 17.68 g/m^2/day in CTS-7403 at 90 days harvest. The root/shoot dry weight ratio had decreased with aging. The aboveground/leaf biomass ratio had increased with aging.

Height and basal area of the crop had increased with aging. The peak leaf area index values were 7.176 (HUS-304) and 10.178 (CTS-7403) at 105 days hervest. Relative growth rate and net assimilation rate of the crop had dereased with aging. The leaf area ratio had increased in early vegetative phase and had decreased afterwards till maturity. The specific leaf area ratio had decreased with aging.

The nutrient concentration and uptake were found to vary with aging. The trend of nutrient concentration and uptake recorded at final harvest was Ca > N > P > K > Na. The nutrient accumulation was found to be dependent upon the dry weight and per cent concentration of the nutrient. The following trends of nutrient accumulation were recorded at final harvest.

Nitrogen

HUS-304 Capitulum > Stem > Dead > Leaf > Root
CTS-7403 Capitulum > Stem > Dead > Leaf > Root

Phosphorus and Potassium

HUS-304 Capitulum > Dead > Stem > Root > Leaf
CTS-7403 Capitulum > Stem > Dead > Root > Leaf

Sodium

HUS-304 Capitulum > Dead > Stem > Leaf > Root
CTS-7403 Dead > Capitulum > Stem > Root > Leaf

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Calcium

HUS-304 Stem > Dead > Capitulum > Leaf > Root
CTS-7403 Stem > Dead > Capitulum > Leaf > Root

Calorific values were found to be ranging between 2948.29 and 6187.30 cal/g in HUS-304 and 3076.40 and 5850.30 cal/g in CTS-7403. The maximum net production efficiency was found to be 1.91% in HUS-304 and 2.80 % in CTS-7408 at 105 days of growth period.

Nitrogen (20, 40 and 60 kg/ha) and phosphorus 10.20 and 30 kg/ha) were given to plants separately. It was found that the application of nitrogen and phosphorus fertilizers had affected dry matter accumulation; height, seed production and oil content. All these parameters were found to be increasing with the application of increasing doses of nitrogen and phosporus. However, nitrogen application was found to be more effective than phosporus.

Intraspecific interference was pronounced plant height was found to be increasing when plants were grown densely. Dry matter production, seed production and oil content were adversely affected by plants grown close to each other due to self generated demands of natural resources.

Crude fibre content in the plant material was found to be increasing with age. Oil percentage was found to be 35.38% (HUS-304) and 31.23% (CTS-7403). Starch was found to be absent in the mature seeds of both the cultivars.

GENETICS OF NITROGEN FIXATION AND HETEROCYST DIFFERENTIATION IN THE BLUE-GREEN ALGA (CYANOBACTERIUM) *GLOEOTRICHIA GHOSEI* SINGH

A. K. Mishra

Sup. *Dr. D. N. Tiwari*

The present investigation views at some genetical aspects of nitrogen fixation and heterocyst differentiation in a local isolate of the blue-green alga (Cyanobacterium) *Gloeotrichia ghosei* Singh. The clonal population raised from a germinating spore has been considered as the parent population throughout the investigation.

Aerobically grown nitrogen-fixing filaments of the parent alga were characterized by the whip-like filamentous morphology together with the

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differentiation of basal heterocysts, followed by the filaments with cells of decreasing size. In contrast, polarity as well as heterocyst differentiation were lost in a variety of combined nitrogen sources (i.e., NO_3^-,NH_4^+ and amino acids like glutamine, serine, aspartic acid and tryptophan) which otherwise supported maximum algal growth. Thus, polarity in *Gloeotrichia* filaments possessing basal heterocysts, which presumably fixed nitrogen, and its disappearance in combined nitrogen suggests that it is consequence of a gradient of nitrogenous substances. MSO (L - methionine - DL - sulfoximine) inhibited N_2 growth of the alga without causing the excretion of detectable NH_4^+ in the culture medium. Heterocysts formed in the filaments got detached and the latter remained non-polar. Growth and uptake of NO_3^- or NH_4^+ in the alga was also inhibited by MSO up to 6 days but soonafter both the processes began simultaneously, indicating the reversible action of MSO. Also, addition of glutamine to the MSO medium reversed the effect of MSO on algal growth.

Mutants of *G. ghosei* defective in nitrogen-fixing ability (Nif^-) and heterocyst differentiation (Het^-) were isolated following NG (N – methyl – N'nitro – N – nitrosoguanidine) and UV (ultraviolet) mutagenesis. NG proved to be a more effective mutagen than UV but the use of chloramphenicol with mutagenic treatments resulted in recovery of more mutants although 'penicillin enrichment' method, used for screening Nif^- mutants, considerably enhanced the mutation frequency. Mutagenized populations immediately used for isolating Nif^- mutants resulted in the production of abnormal colonies which, when isolated and grown in NO_3^- medium for 2-3 generations produced two kinds of developmental mutants defective in nitrogen fixation (Fil^s and Fil^1 strains). In contrast, the mutagenized population when allowed to segregate for 30 days, produced a variety of Nif^- mutants which could be grouped, when grown on N_2 – medium, into three developmental phenotypes viz., (i) usually long filaments capable of differentiating into basal heterocyst and apical tapering (Fil^1 Het^+), (ii) long filaments, like Fil^1 Het^+ strain, capable of differentiating into chains of intercalary heterocysts at regular intervals with the development of intercalary polarity between two heterocyst points (Fil^1 Het^{++}), and (iii) undifferentiated nostocacean type filaments with complete loss of polarity (Pol^- Het^-). The combined sources of inorganic (NO_3^-or NH_4^+) and organic nitrogen (amino acids like glutamine, serine, aspartic acid and histidine) which supported maximum growth of Nif^- mutants, completely suppressed the development of heterocyst and polarity in the filaments of the former two mutants. However, chains of heterocysts formed in the filaments of Fil^1 Het^{++} strain in N_2 – medium served as weak points for fragmentation of filaments into small pieces, each possessing a few hetero-

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cysts at one end and polarity at the other. Such cells identified as heterocyst had polar thickening characteristic of heterocysts. Transfer of filaments, with heterocysts, to NO_3^-, NH_4^+ or amino acid medium resulted in cent per cent regression of heterocyst *in situ*, ultimately releasing undifferentiated germlings. Growth and total nitrogen measured for these mutants under combined nitrogen-free, aerobic, reducing and anaerobic growth conditions, showed no gain compared to the nitrogen-fixing parent alga, which showed much gain in total nitrogen only under aerobic conditions.

Observations on growth characteristics of Nif$^-$ mutants in the presence of amino acids indicate that certain amino acids like glutamine, serine, aspartic acid and histidine, can very well serve as sole source of fixed nitrogen for their growth. However, these mutants differed from the parent alga in utilizing histidine as a fixed nitrogen but not the tryptophan. MSO combined NO_3^- or NH_4^+ media inhibited the mutant growth and induced formation of heterocyst and polarity in the filaments of Fil^1 Het$^+$ and Fil^1 Het^{++} strains characteristics to their development observed in N_2 medium. Addition of glutamine or methionine or both to the MSO medium reversed the growth inhibitory effect of MSO in the Nif$^-$ mutants. Since tryptophan was unable to serve as nitrogen source for the growth of Nif$^-$ mutants, it did not show reversal of Aza – T which inhibited mutant growth in the presence of organic and inorganic nitrogen sources. MSO inhibition of growth and uptake of NO_3^- and NH_4^+ in Nif$^-$ mutants was also found to be reversed but only after a lag of 3-6 days. In Aza-T medium filaments of mutants were fragmented and ultimately lysed.

Reversion of Nif$^-$ to Nif$^+$ character was obtained in Fil^1 Het^{++} strain but not in others. Some revertants were produced both spontaneously as well as after treatments with NG, UV and EMS (Ethyl-methane sulfonate). Acriflavin could not induce such reverse mutations. Nif$^+$ revertants restored the nitrogen fixing competence and whip-like filamentous morphology characteristic of the parent strain but differed in the formation of naked spore (without thick envelop) and mucilage secretion.

Nif$^-$ mutants were found to be comparatively sensitive to various antibiotics and mutagens compared to the parent alga. Attempts to isolate drug-resistant mutants from such mutants were unsuccessful. However, cultures of Fil^1 Het^{++} treated with mutagens produced several kinds of pigment and morphological mutants. Five pigment mutants were isolated. Two pigments mutants induced by UV showed dominance of either blue pigment (phycocyanin), (blue strain, B-1) or red pigment (phycoerythrin), (violet strain, V-1) while NG induced pigment mutants were characterized by blue-green (blue strains B-3 and B-7) and brown pigment (brown strain

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– Br - 6). Morphologically, they were identical to Fil[1] Het++ strain. Non-polar filamentous mutants (ST-4, ST-10) induced by NG and EMS lacked both heterocyst and polarity. Blue-pigment mutants exhibited a characteristic absorption peak at 610 nm while violet or brown pigment mutants showed at 550 nm only compared to Fil[1] Het++ strain which showed two peaks at 550 and 610 nm. In contrast, short trichome mutant (ST-4) showed an absorption peak of water soluble pigments at 660 nm, indicating for the presence of allophycocyanin.

PHYTOTOXICITY OF SULPHUR DIOXIDE AIR POLLUTION AND ITS CONTROL

Pradeep Kumar Nandi Sup. *Dr. D. N. Rao*

The present study was undertaken to assess the effects of relatively low concentrations of SO_2 on some selected crop plants an l also to eva uate the efficacy of certain chemicals as ameliorating agents for SO_2-toxicity. With these aims in view, three separate experiments were conducted as mentioned below :

(i) Effects of 0.25 and 0.5 ppm SO_2 on *Oryza sativa* plants

(ii) Effects of 0.02*M* potassium ascorbate ($C_6H_7O_6K$) spray on 0.1 and 0.25 ppm SO_2-exposed *Vicia faba* plants

(iii) Effects of 0.5% lime water [$Ca(OH)_2$] and 0.5% sodium benzoate (C_6H_5 COONa) sprays on 0.25 ppm SO_2-exposed *Vigna sinensis* plants

Experiment I :

Rice (*Oryza sativa*) plants were grown during rainy season in control (C), T_1 and T_2 beds-each of 1.5 × 1.5 m size. Plants of T_1 bed were exposed to 0.25 ppm and that of T_2 bed to 0.5 ppm SO_2 for 1.5 hrs daily between 40 and 60-day ages, when the plants were in the phase of tillering. After a recuperation period of 10 days, these plants were again exposed to the above SO_2 concentrations between 70-80 day ages, coinciding with the period of ear emergence and flowering. Plant and soil samples from C, T_1 and T_2 beds were collected at 40, 50, 60, 70, 80 and 90-day plant ages.

The soils of SO_2-exposed beds in comparison to the control, showed increases in organic carbon and decreases in pH and N, P, K and Ca levels in proportion to So_2-concentrations.

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The visual injury symptoms of tip burning and interveinal chlorosis and necrosis of leaves were first noted in T_2 plants, which increased with cumulative SO_2-doses. Transpiration rate and water saturation deficit in plants increased after exposure to SO_2, the maximum increase being in 0 5 ppm SO_2-exposed plants. With respect to the control, the increases of S and decreases of N, P, K and Ca levels in T_2 plants were more than T_1 plants. At early stages of growth, the S-content was maximum in leaves and minimum in roots but with advancing age of plants this situation was reversed. The N/S ratio and leaf-extract pH also decreased maximally in leaves of SO_2-exposed T_2 plants. With respect to the control, decreases in total chlorophyll and carotenoid contents were also more in T_2 than those in T_1 plants. From the chl *a*/chl *b* ratio, which was higher in SO_2-exposed plants, it appeared that chl *b* of rice plants was more sensitive to SO_2 than chl *a*. It was also noted that changes in levels of metabolites in treated plants were positively related to SO_2-concentrations. Quantitatively the metabolites like starch, ascorbic acid and protein were reduced and soluble sugars increased in SO_2-exposed plants. Increase of reducing sugar and decrease of ascorbic acid, in proportion to SO_2 concentration in T_1 and T_2 plants suggested a possible inhibition of ascorbic acid synthesis in them. Further, on the basis of distinct correlation between peroxidase activity and ascorbic acid contents, it is inferred that there was oxidation of ascorbic acid in SO_2-exposed plants. At increasing cumulative SO_2-doses, the activity of catalase decreased but that of peroxidase increased. A negative correlation between catalase and peroxidase activities, suggested enzymatic changes resulting from the breakdown of tetrametric catalase into monomers showing peroxidase like activity, resulting in enhanced peroxidase mediated oxidation of chlorophyll. With respect to the control, the SO_2-exposed plants showed reductions in their root and shoot lengths, numbers of leaves, tillers and ears, and phytomass and productivity levels; the maximum reduction being in case of 0.5 ppm SO_2-exposed plants.

The SO_2-exposure of plants led to decreases in economic yield and deterioration in quality of grains, especially with respect to their weight, calorific and nutritive values.

Experiment II :

In this experiment, an attempt was made to test the efficacy of potassium ascorbate as an antidote against SO_2-phytotoxicity.

Broad bean (*Vicia faba*) plants were raised during winter in 1×1m beds, referred to as C, CS, T_1, T_1S, T_2 and T_2S beds. Plants T_1 and T_1S beds were exposed to 0.1 ppm and those of T_2 and T_2S beds to 0.25 ppm SO_2 for 1.5 hrs daily for 60-days between 40 and 100-day of their ages.

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Plants of CS, T_1S and T_2S beds were sprayed with 0.02*M* potassium ascorbate aqueous solution at 45, 60, 75, 90 and 105-day ages. The plant and soil samples from each bed, collected at 40, 55, 70, 85, 100 and 115-day plant ages, were analysed for different parameters.

There were increases in organic carbon and decreases in pH and N, P, K and Ca contents of soils of T_2 and T_2S beds. Such changes in T_1 and T_1S beds were not so pronounced and the nitrogen in soils of these beds remained more or less at the same level throughout the experimental period.

In the SO_2-exposed plants, characteristic visual injury symptoms first appeared in T_2 plants, which increased at increasing cumulative SO_2-doses. The level of injury at any given age in T_1S and T_2S plants was less than that in T_1 and T_2 plants, respectively. With age, the injured leaves were shed maximally in T_2 plants.

The increases in transpiration rate and water saturation deficit were higher in SO_2-exposed plants than those in SO_2-exposed+$C_6H_7O_6K$ sprayed ones. The leaf-extract pH and N, P, K and Ca levels in SO_2-exposed plants decreased in proportion to SO_2-doses. However, these decreases in T_1S and T_2S plants were comparatively less than those in T_1 and T_2 plants, respectively. In SO_2-exposed plants the decrease of nitrogen was more in roots than in leaves. The S-levels in SO_2-exposed plant parts were higher than in those of the control; the increase being maximum in leaves of T_2 and minimum in those of T_1S plants. Similarly, decrease in N/S ratio was maximum in T_2 and minimum in T_1S plants. In all the SO_2-exposed plants, the levels of chlorophyll, carotenoids, starch and ascorbic acid were lower and of soluble sugars higher than those in the control. These changes were maximum in T_2 and minimum in T_1 S plants. The chl *a*/chl *b* ratios in T_1 and T_2 plants were lower and those in T_1S and T_2S plants higher than the control. This indicated that SO_2-induced destruction of photosynthetic pigments in potassium ascorbate sprayed plants was of a lower magnitude than in the unsprayed ones and that this chemical provided some protection to chl *a*.

In T_1S and T_2S plants the increase in phenol and soluble sulphydryl contents were less than those in T_1 and T_2 plants. The changes in catalase and peroxidase activities of SO_2 – exposed broad bean plants were similar to those of SO_2 – exposed rice plants but the level of activities in T_1S and T_2S plants were less pronounced than those in T_1 and T_2 plants. It was suggested that in SO_2 – exposed as well as potassium ascorbate sprayed plants, the phenol and peroxidase synthesis was reduced which prevented

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chlorophyll oxidation in them. Further, relatively higher levels of ascorbic acid in T_1S and T_2S plants helped scavenging superoxide radicals and protecting chlorophyll from oxidation.

The plant growth, in terms of lengths of root and shoot, numbers of leaves, flowers, fruits and nodules, phytomass accumulation and net primary productivity of SO_2 – exposed plants, was less than that of the control. At any given age, the growth performance of CS plants was the best of all but it was most affected in T_2 plants.

From the seed quality data of all SO_2 – exposed plants, it is evident that the calorific and nutrisive values of seeds of T_1S and T_2S plants were better than those of the seeds of T_1 and T_2 plants.

Experiment III :

In this experiment, an attempt was to test the efficacy of lime water [$Ca(OH)_2$] and sodium benzoate (C_6H_5COONa) as agents, ameliorating SO_2 effects.

Cowpea (*Vigna sinensis)* plants were raised during summer months in six beds each of 1.5 × 1.5 m size, referred to as C, CC, CS, T, TC and TS beds. Plants in T, TC and TS beds were exposed to 0.25 ppm SO_2 for 1.5 hrs daily, between 30 and 70-day plant ages. At 35, 45, 55 and 65-day ages, the plants of CC and TC beds were sprayed with 0.5% aqueous solution of $Ca(OH)_2$ and those of CS and TS beds with 0.5% sodium benzota solution. Plant and soil samples from each bed were collected at 30, 40, 50, 60. 70 and 80-day plant ages for analyses. The pH, and N, P and K levels in soils of SO_2 – exposed beds were generally lower than those of soils of control beds. The Ca levels in SO_2 – exposed soils also declined, but such a change in TC bed soil was delayed.

Except for T plants, no foliar injury appeared in other SO_2 – exposed plants. In all the SO_2 – treated plants, the S levels were more but N, P, K and Ca levels were less than of the control. The decrease of Ca in TC plants was less than that of T and TS plants. The increase is S content and decrease in leaf-extract pH were more in T than that in TC and TS plants. With respect to the control, the decrease of nitrogen in T plants was more in roots than in leaves, but these decreases were relatively less in TC and TS plants. The N/S ratio decreased in all the SO_2 – exposed plants, the decrease being maximum in T plants. Relative to the control, decreases of protein in 70-day old T, TC and TS plants were 32.5, 9.3 and 13.3% and increases of amino acid 78.9, 33.6 and 21.0%, respectively. These change suggest that nitrogen metabolism in TC and TS plants was affected less than that in T plants. Similarly, the levels of chlorophyll and

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carotenoids also decreased maximally in T plants than that in TC and TS plants. The chl *a*/chl *b* ratio in SO_2 – exposed plants did not show any definite trend which suggested that these pigments remained equally sensitive to SO_2.

The responses of SO_2 – exposed cowpea plants, with respect to change in starch, ascorbic acid, soluble sugars, phenols and soluble sulphydryl contents and activities of catalase and peroxidase, were similar to those noted in case of rice and broad bean plants. However, thess responses were more significant in T and less in TC and TS plants. Relative increases of phenol content was maximum in T and minimum in TS plants, which suggested that possibly benzoate checked the SO_2 – induced synthesis of phenol in them through inactivation of phenylalanine ammonia lyase activity, thereby reducing cellular injury.

The growth rates of C, CC and CS plants were higher than those of T, TC and TS plants. With respect to the control, decreases in phytomass accumulation in 80-day old T, TC and TS plants were 40.7, 29.7 and 24.5%, respectively. The extent of seed quality deterioration among SO_2 – exposed plants were maximum in T and minimum in TS plants.

It was noted that though lime water and sodium benzoate failed to stimulate growth of control plants, they did provide protection to some extent to SO_2 – exposed plants, which was evident from the better growth and absence of injury symptoms in these plants.

On the basis of these experiments, it may be concluded that long-term SO_2 exposure may cause injury to plants through unfavourable changes both in plant and soil systems that SO_2, at concentrations even as low as 0.1 ppm, may produce several physiological disturbances in plants leading to premature senescence, development of injury symptoms, reduction in growth and yield and deterioration in quality of seeds; that the extent of foliar injury may not be a reliable indicator of production losses in SO_2 - exposed plants, for example, though there was more foliar injury in case of rice but the reduction in dry matter was greater in broad bean and cowpea plants having lesser foliar injury; that the nitrogen metabolism in SO_2-exposed legumes is affected more, possibly due to decreases in growth and development of nodules; that it is possible to ameliorate to some extent the SO_2-induced plant injuries with the help of certain chemical sprayed; that the ameliorating efficiency of potassium ascorbate against SO_2-toxicity in broad bean is quite significant, that lime water and sodium benzoate may help cowpea plants to mitigate SO_2-toxicity and protect these plants against SO_2-pollution and the latter chemical being a better ameliorating agent than the former.

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STUDIES ON THE MICROFUNGI OF GUAVA PLANTATION IN CHIRAIGAON OF VARANASI

R. R. Pandey Sup. *Dr. R. S. Dwivedi*

Guava, (*Psidium guajava* L.), a native of tropical American, cultivated in India as a cash crop, is a much favoured valuable fruit for its rich vitamins and nutritive values. *C. gloeosporioides* and *P. psidii* along with a number of pathogenic forms causing leaf and fruit diseases have been reported to cause substantial reduction in fruit production as well as fruit quality causing considerable economic loss to the growers. This particular crop plant also suffers severely due to the attack of a pathogen *Fusarium oxysporum* f. sp. *psidii* causing wilt disease.

During surveys of guava plantation we found that the incidence of pathogen on the leaf surface fluctuates considerably in different seasons and this fluctuation may be either due to the weather changes or to other phylloplane mycoflora involved in some way suppressing the pathogen. Therefore, it was necessary to determine the other phylloplane fungi in controlling severity by the disease biologically. Keeping these points in view the present study was undertaken as a first step to determine in detail the microfungi of guava plantation with reference to pathogenesis, fungicidal and biological control. The summary and conclusions derived from the present study are given below.

I. A total of 67 species of fungi were screened in three seasons from leaf surface of guava. These constituted 5 Phycomycetes, 5 Ascomycetes, 2 Sporobolomyces and 55 Deuteromycetes. The average number of composite phylloplane fungi was maximum in rainy season followed by winter and minimum in the summer. A number of species of fungi were common in all the three seasons. Season-wise 3 main groups viz., exclusive season fungi, season sensitive fungi and season insensitive fungi were identified. Fungal species sensitive to seasonal fluctuations included *Aureobasidium pullulans*, *Cladosporium cladosporioides*, *Colletotrichum gloeosporioides*, *Pestalotia psidii*, Pink yeast, *Arthrinium phaeospermum* and white yeast.

Distribution pattern of fungi (cm^{-2}) at different development stages of leaf increased from opening bud-stage to the senescent stage, while at the leaf fall stage a general decline in fungal population was noted in all the three seasons. The bud and newly expanded leaves were colonized by a limited range of fungi such as *Alternaria alternata*, *Aureobasidium pullulans*, *Aspergillus niger*, *Cladosporium cladosporioides* and *Epicoccum purpurascens*. Pink yeast and white yeast were also recorded frequently during rainy and winter season while they were completely absent in the

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summer. The number of fungal species was maximum at leaf senescent stage in each season. Qualitatively four categories of fungi were recognized which tended to be associated with leaves of different ages. The 'early leaf fungi' appeared at bud and newly expanded leaves; 'mature leaf fungi' at mature leaves; 'dying and dead leaf fungi' at senescent and freshly fallen leaves while 'consistently associated fungi' were isolated from bud to the last stage of leaf age. Some forms such as *Robillarda sessilis*, *Pestalotiopsis desseminata*, *Stemphylium* sp., *Stachybotrys* sp. and *Trichoderma* sp. were isolated at senescent and dying leaves, suggesting their involvement in the decomposition of leaf at later stages.

The maximum number of fungi was isolated by dilution plating followed by moist chamber technique. Lesser number of fungi was associated with the washed disks revealing that internal colonization is a specialized character. Species of fungi such as *Memnoniella echinata*, *Curvularia senegalensis*, *Stachybotrys* sp. and *Torula* sp. were only isolated by the moist chamber method. A significant variation in the number of fungi at different stages of leaf and the methods of their isolation from the phylloplane of guava was observed.

II. A total of 28 fungal species was encountered during four samplings of different floral parts of guava employing dilution plate and washed disk method. A significant variation was obtained among the distribution of fungi at various floral parts. Species of fungi namely, *Alternaria alternata* *Aureobasidium pullulans*, *Cladosporium cladosporioides*, *Drechslera australiensis*, *Epicoccum purpurascens* and *Fusarium* sp. were highly prevalent in all the samplings of floral parts.

III. The asromycospora of guava orchard is found to be very rich in its composition. The present study reveals that different fungi showed their maxima-minima in different seasons. The highest fungal species were isolated in September followed by October and the lowest in the month of December. *Alternaria humicola*, *Bipolaris spicifera*, *Dendrophoma* sp., *Hormiscium* sp. *Monilia sitofila* and *Syncephalastrum racemosum* were only isolated from the air.

IV. Twenty fungi were found to be associated with unsterilized and sterilized health and infected seeds obtained from healthy and rotted fruits of guava by Agar plate and Blotter techniques. *Botryodiplodia theobromae*, *Colletotrichum gloeosporioides*, *Pestalotia psidii* and *Phoma glomerata* were isolated from sterilized infected seeds. The pathogenecity of *B. theobromae*, *C. gloeosporioides* and *P. psidii* was confirmed on guava fruits under field and laboratory conditions by Pin-prick and Deep-wound methods of inoculation.

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V. Soil mycofloras were isolated to study, specially, the dynamics of *Fusarium oxysporum* f. sp. *psidii* in relation to other mycoflora. The most common and dominant genera were *Aspergillus*, *Fusarium* and *Penicillium* which appeared in all the three depths of soil i. e., 0-15 cm, 15-30 cm and 30-45 cm. Other frequent genera were *Alternaria*, *Cladosporium*, *Curvularia*, *Drechslera*, *Gliocladium* and *Thielavia*. Members of these major genera along with sterile black mycelia constituted 46 % of the total isolates. *Paecilomyces* sp., *Humicola* sp., and *Trichoderma* sp. occurred at low frequencies. Out of six species of *Fusarium*, *Fusarium oxysporum* f. sp. *psidii* showed the highest frequency closely followed by *F. solani* and *F. semitectum*. The highest fungal population at all the three depths was observed in July and another in November. Fungal population/gm dry weight was minimum in May for depth A, April for depth B and in September for depth C. Positive correlation between organic matter content of soil and fungal population at all the three depths studied is statistically significant for depth A and B but in case of depth C it was insignificant. The number of fungi decreased with increase in soil depth. Moisture content and organic matter favoured the growth of fungal population.

VI. Three pathogens namely, *Colletotrichum gloeosporioides* and *Pestalotia psidii* from the foliage and *F. oxysporum* f. sp. *psidii* from the roots of guava were isolated in the present study. *Pestalotia psidii* was prevalent in all seasons but it caused several diseases in winter and rainy seasons. The incidence of *C. gloeosporioides* was recorded much in rainy and less in winter season. *F. oxysporum* f. sp. *psidii* caused severe disease mostly in rainy season. Histopathological studies of the affected roots revealed the presence of intracellular growth of mycelium inside the lumen of xylem vessels.

VII. Effect of two fungicides namely, Benlate and Captan in rainy, and four viz. Benlate, Captan, Dithane M-45 and Phygon-XL in the winter season at 500, 1500 and 3000 ppm concentrations on the population dynamics of pathogenic forms and non-pathogenic forms was studied under *in vivo* condition. The treatment of chemicals was given thrice in the rainy season and five times in the winter season to compare the effect of number of spray on distribution of fungi. Benlate was found most effective in declining the population of pathogens and checking further disease incidence. However, Benlate was effective only at the schedule of three successive foliar applications. The application of Captan did not check the population dynamics of *P. psidii* as effectively as Benlate but it had marked adverse effect on many of the phylloplane mycoflora. A significant decrease in the number of fungal species colonizing Phygontreated leaves was observed. Some dominant phylloplane fungi viz. *Alternaria alternata*,

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Aspergillus niger, *Curvularia lunata*, *Drechslera australiensis* and *Penicillium citrinum* showed less decline in their distribution of *P. psidii* also showed high degree of tolerance to the chemicals applied since it frequently colonized phylloplane even after fifth sprays. However, the population of both the pathogens in terms of number of colonies recorded per cm^2 leaf area decreased with the increase in number of sprayings of the fungicides. As to the concentrations of chemicals a higher degree of inhibition in the population of the fungal species was obtained with the increase in dose of chemical application. 3000 ppm of the chemicals was generally suitable to cause appreciable decline in pathogen's population.

VIII. Species of fungi which comprised frequent isolates of the phylloplane of guava were screened out to assay their antagonistic activity against two pathogens viz. *C. gloeosporioides* and *P. psidii* both *in vivo* and *in vitro*.

Culture filtrates of *Aspergillus nidulans*, *F. oxysporum* and *Penicillium oxalicum* caused more than 50% inhibition in colony growth of *C. gloeosporioides*. However, *C. roseo-griseum*, *Myrothecium roridum*, *Penicillium citrinum* and *Trichoderma harzianum* were also superior in reducing the growth of *C. gloeosporioides*. The metabolites of *F. oxysporum* followed by *A. alternata*, *A. terreus*, *C. roseo-griseum*, *M. roridum* and *Penicillium oxalicum* appeared to be the most effective in causing reduction in radial growth of *P. psidii*. There was statistically significant variation in inhibition in growth of both pathogens with respect to the treatment of culture filtrates of different phylloplane fungi individually.

Volatile emanated from the cultures of *Aspergillus nidulans* and *Penicillium oxalicum* followed by *Curvularia lunata*, *Fusarium semitectum* and *Penicillium citrinum* produced marked degree of inhibition in the growth of *Collectotrichum gloeosporioides*. Slight stimulation in growth of test pathogen was recorded with the volatiles of *Cladosporium cladosporioides*, *C. herbarum*, *Epicoccum purpurascens*, *Nigrospora sphaerica* and *Papulaspora* sp. In case of *Pestalotia psidii* effective inhibition (more than 30%) was observed with tne culture volatiles of *Cephalosporium roseo-griseum*, *Trichoderma harzianum* and *Fusarium oxysporum*. Inhibition in growth with respect to lengthening of incubation receeded correspondingly. Optimum effective activity of volatiles was, in general, noticed after 48 hrs incubation. Such an effect is apparently connected with either susceptibility of *C. gloeosporioides* and of *P. psidii* to volatile during early phase of growth or to the better production of volatiles during actively growing stages of the fungus.

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Interactions in dual cultures between the pathogens and some leaf inhabiting fungi were found antagonistic against a number of phylloplane fungi. An appreciable degree of inhibition of *C. gloeosporioides* was obtained with *C. cladosporioides* and *Fusarium oxysporum* (Grade E). Complete inhibition in growth of *P. psidii* was discerned when juxtaposed with *A. flavus*, *A. niger* and *T. harzianum*.

Interactions between phylloplane fungi and pathogenic forms on leaf surface revelaed suitable antagonists such as *Aureobasidium pullulans*, *Aspergillus terreus*, *Cladosporium cladosporioides* and *Fusarium oxysporum* in case of *Colletotrichum gloeosporioides* and *A. terreus*, *A. niger*, *P. chrysogenum* and *T. harzianum* in case of *P. psidii*. The propagules of *A. alternata C. roseo-griseum* also caused appreciable reduction in lesion size of *P. psidii*. The minimum inhibitory effect was noticed by *Drechslera australiensis* in case of *C. gloeosporioides*. Increasing concentrations of spore suspension resulted in enhancement of inhibition in lesion. Statistically a significant variation was obtained among the treatment with propagules of different phylloplane fungi and their different concentrations on the lesions caused by both pathogens individually.

The guava wilt caused by *F. oxysporum* f. sp. *psidii* was specially considered in the present study for its control. Fungicides-Bavistin, Benlate, Captan, Dithane M-45 and Phygon-XL; antibiotics of Griseofulvin and Mycostatin; heavy metals-$CdCl_2$, $CoCl_2$, $CuSO_4$, $HgCl_2$ and $SnCl_2$ showed inhibition effects on the growth of the pathogen *in vitro*. It is suggested that these chemicals may be used for control of the wilt of guava.

STUDIES ON NODULATION OF GREEN GRAM IN RELATION TO SOIL PHYSICO-CHEMICAL AND BIOLOGICAL ENVIRONMENT

Mutum Shyamkesho Singh Sup. *Dr. B. Rai*

The present work comprises the study of the effect of some important soil physical, chemical and biological factors on the growth and nodulation of green gram (*Vigna radiata* (L) Wilczek. var. type 44). The microbiology and the pattern of weight loss and nitrogen disappearance from decomposing leaf, stem and root of the test crop were also studied after harvest period. The main findings during the course of study and some important conclusions drawn from the results are summarized below.

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A *Rhizobium* strain was isolated from the nodules of the test plant using standard microbiological techniques. When the isolated strain was inoculated to the seeds of green gram, efficient nodulation and plant growth were observed. Addition of KNO_3 in soil greatly reduced the nodulation.

Different soil textures, obtained artificially, did not affect the plant growth and nodulation significantly. Soil moisture level greatly affected the nodulation and plant growth. It also influenced the relative growths of shoot and root of the test plant. Near-water-logging condition affected the nodulation process than by low moisture content ($\approx 10\%$ w/w).

Initial soil pH (range 5.5 – 8.5) affected the nodulation process but not the plant growth. The effect of acidic pH was more pronounced than that of alkaline pH. In culture medium *Rhizobium* showed different survivality rate at different pH values.

Among three fertilizers examined (super phosphate, potassium chloride and NPK), P and K fertilizers stimulated plant growth and nodulation as well as per cent nitrogen content of the test plant at low concentrations (0.1%) but the higher concentrations inhibited all the parameters. At 1.0% level of P the plants were killed at the seedling stage. NPK at all used concentrations greatly stimulated nodulation and growth of green gram. Thus, in the field application of proper combinations of the three nutrients may be important for better pulse production.

PCNB was very toxic to nodulation and growth of the plant and also to *Rhizobium* growth. Thimet at 50 ppm increased the shoot dry weight in comparison to the control. It shows a compatible result possibly for field application if not stimulated the nodulation. Nitrogen also reduced the growth parameters, but because of its low doses recommended in the field it may not be harmful for agronomic application. On *Rhizobium* growth also PCNB was most toxic in comparison to the other two pesticides.

Among the three heavy metal compounds, $CuSO_4$ and $ZnSO_4$ were found to be stimulatory at 0.01 millimoles/Kg soil concentration but the higher concentrations showed detrimental effect. $HgCl_2$ at all concentrations inhibited plant growth and nodulation. 1.0 millimoles/Kg soil of $HgCl_2$ was fatal for the plants. The three compounds also showed different toxicity to *Rhizobium* growth. At 1.0mM of $ZnSO_4$, 0.1mM of $CuSO_4$ and 0.01mM of $HgCl_2$ 100% mortality of *Rhizobium* was observed. Therefore, in the field low levels of Zn and Cu application or selection of fertilizers which incorporate the trace elements may give better plant pro-

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duction especially when their availability is limited. However, care should be taken to check application at their toxic levels.

In the rhizosphere and non-rhizosphere soil of the test plant different microbial population were observed both quantitatively and qualitatively. The total microbial count in the root region was influenced by the plant growth stages. The highest population of fungi was recorded during the preflowering stage whereas the highest increase of actinomycetes was recorded during preflowering to fruiting stage. For bacteria the highest population was noted at the flowering stage.

The R/S ratio of different microbial population also differed according to the type of microorganisms and the growth stages of the plant. The highest R/S ratios for bacteria and actinomycetes were observed during the flowering stage, while that of fungi was during preflowering stage.

Ten fungal species, viz., *Aspergillus flavus*, *A. niger*, *A. terreus*, *Curvularia lunata*, *Fusarium oxysporum*, *Papulaspora* sp., *Penicillium citrinum*, *Rhizoctonia solani*, *Rhizopus nigricans* and *Trichoderma viride*, which were more frequently isolated from the root region of the test plant were selected for further studies.

Nodule extract of green gram stimulated the radial growth of the ten fungal species. However, the growth behaviours of the fungal species, especially the growth rate, seems to influence the stimulatory effect of the nodule extract. Among the fast growing fungi i.e., *A. flavus*, *C. lunata*, *F. oxysporum*, *papulaspora* sp., *R. solani*, *T. viride*, the highest stimulatory effect was observed during the early incubation period (24 to 48 hrs). In case of slow growing fungi i. e., *A. terreus* and *P. citrinum* the stimulatory effect was prolonged upto late incubation period.

Culture filtrates of the above fungal species were also tested for their effects on the growth of *Rhizobium*. The most inhibitory effect on survival of *Rhizobium* was exhibited by culture filtrate of *A. terreus*, as no *Rhizobium* colony was developed even at 1% concentration of the fungal metabolite. Complete mortality of *Rhizobium* was recorded at 20% *P. citrinum* filtrate and 10 and 20% of *T. viride* filtrate. Culture filtrates of *Papulaspora* sp., *R. solani*, and *R. nigricans* were least inhibitory to the *Rhizobium*. Culture filtrates of *A. flavus*, *C. lunata* and *F. oxysporum* were also comparatively inhibitory to the *Rhizobium*.

When the hyphal mats of the ten fungal species are amended in sterile soil, the nodulation and plant growth were adversely affected except in case of *A. flavus*, *Papulaspora* sp. and a combination of them. However, when hyphal mats of all the ten fungal species were combinely amended,

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the reduction in nodulation was insignificant. Thus, the implications of these findings are that, some of the most common saprophytic soil fungi such as *A. niger* and *A. terreus* may hinder the development of an effective population level and eventually the nodulation and nitrogen fixation, when the fungi are present in higher population in the soil. However, under natural conditions due to competition with other microorganisms the population of a particular fungal species may not be too high to completely inhibit the nodulation. Nevertheless, when a *Rhizobium* strain is introduced in a new environment, its competitive saprophytic ability and tolerance against other antagonist microorganisms may be of significant value in establishing its effective population level in soil and successful nodulation.

The nitrogen retention of different parts of green gram during different growth stages and their decomposition after harvest stage has also been studied. The highest per cent nitrogen content of leaf, stem and root was recorded during the seedling stage, which was gradually reduced with plant age. In all the stages leaves were containing higher nitrogen concentration than the roots, the least being in case of stem. Among all the plant parts nodules were containing the highest per cent nitrogen. During fruiting stage the per cent nitrogen content of the other plant parts were considerably reduced. At the senescent stage the leaves were still containing comparatively higher per cent nitrogen (2.86 %) in comparison to stem (1.22%) and root (1.49%).

Thus, by the common practice of removing the whole above-ground plant parts during harvest a considerable amount of nitrogen may be lost from the original field along with the harvested plant parts.

During decomposition of the plant parts the highest rate of weight loss was recorded in leaf materials which was followed by stem and the least being in the roots. In the same way the per cent nitrogen contents of the three materials during different stages of decomposition was also influenced by type of the materials and their original nitrogen content. Regarding the loss of nitrogen from the decomposing plant residues, the highest rate of nitrogen loss was recorded during the early stage of decomposition. More than 85% of the original total nitrogen was lost from the leaf samples for 150 days of decomposition. In case of stem and root materials the total loss of nitrogen was nearly 70% of the original total nitrogen for 195 days of decomposition.

In the field conditions decomposition rate may be higher than that recorded in the litter bag study because of low accumulation of the plant residues. Also the lost nitrogen from the decomposing plant residues may

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not directly enter into the available soil nitrogen pool because of its immobilization by microorganisms. Even if they enter into the soil nitrogen pool they may be lost from the original site of decomposition by many processes such as leaching, volatilization, etc. Nevertheless, the returning of the harvested plant parts to the field should be encouraged among the farmers because not only it enrich the soil nitrogen but it also likely to improve other important soil properties.

IMPACT OF BISULPHITE ON N_2 FIXING POTENTIAL IN THE BLUE-GREEN ALGA *NASTOC CALCICOLA* BREB

Rajendra Pratap Singh Sup : Dr. *A. M. Singh*

The toxicity of bisulphite to the nitrogen-fixing blue-green alga *Nostoc calcicola* was studied and the results obtained during present course of investigation infer :

(1) The inhibitory effect of bisulphite on growth of *N. calcicola* was found to be pH-dependent. Environmental factors like pH and amino acids were found to regulate the toxic behaviour of bisulphite towards *N. calcicola*. While low pH levels enhanced the toxicity of bisulphite, higher pH levels protected the organism against bisulphite toxicity. Extremely low bisulphite levels (250 ppm) were stimulatory to growth of the test organism. Amino acids like glutamine, aspartic acid, arginine, cysteine and methionine proved antagonistic to bisulphite toxicity at low pH but at higher pH or at alkalinity, only glutamine, aspartic acid, arginine showed protection. Cysteine and methionine, on the other hand, did not show such type of protection. The analyses of pigment contents revealed a high resistance of Chl *a* / carotenoid ratio, while the phycocyanin / Chl *a* ratio showed significant decline in the bisulphite-treated cells. Bisulphite caused bleaching of Chl *a* along with a shifting of absorption band of acetone-soluble pigments by 20 nm only in the blue part of spectrum, accompanied by only a reduction in the respective peak heights. In the red region, there was no sign of band shifting, although a reduction in peak values was clearly observed. The bisulphite-sensitivity pattern of macromolecular synthesis in a decreasing manner, was DNA > protein > RNA > carbohydrates. Methanol-soluble species of carbohydrates in *N. calcicola* cells were less affected than the methanol-

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insoluble ones under bisulphite-stress. Bisulphite inhibited the nitrogen fixation process in the test alga at low pH, but the same concentration was stimulatory to the process at higher pH.

(2) Consumption of nutrients like nitrate, ammonia and phosphate was inhibited by bisulphite in a pH-dependent manner. Bisulphite inhibited the uptake of such nutrients at low pH, but the same concentration of bisulphite enhanced the rate of nutrient uptake at higher pH.

(3) The efflux of vital ions like potassium and sodium could be used as the ideal parameter for assessing the bisulphite toxicity of *N. calcicola*. Efflux of K^+ and Na^+ was pH-dependent; at low pH, the ion loss was more in contrast to high pH conditions. The loss of Na^+ ions seemed to be more sensitive to bisulphite than those of K^+ under similar set of conditions. Loss of ions could be cheked by supplementation of calcium ions, but at the same time, increasing concentrations of phosphate enhanced bisulphite induced ions loss. Na^+ and K^+ loss were relatively less in double distilled water than in the nutrient medium containing inorganic salts. The cells of *N. calcicola* gave positive indications for an efficient buffering system at the extracellular and intracellular levels. External pH (pH of nutrient medium) and internal pH (pH of cell-free extracts) showed a trend towards neutrality when the cells were exposed to either low pH or high pH conditions.

(4) Interaction studies between bisulphite and fluoride, nitrite, calcium and zinc ions were performed in terms of growth of the organism. Bisulphite and nitrite ions interacted synergistically (at low pH) and antagonistically (at high pH). Calcium and zinc ions interacted antagonistically with bisulphite at both the pH levels in contrast to fluoride, which interacted synergistically under high pH as well as low pH regimes. During subsequent additions of zinc, calcium and nitrite ions following pre-exposure of the algal cells to lethal concentrations (250 ppm and 1500 ppm) of bisulphite (at high and low pH levels), only zinc and calcium ions were antagonistic at both the pH levels. Nitrite ions on the other hand, were antagonistic only at higher pH and the degree of antagonism was more marked than during simultaneous additions. Nitrite ions were highly toxic in combination with bisulphite ions even under subsequent additions.

The overall observations point towards the hyper sensitivity of the test alga towards bisulphite. This has been attributable to different dissociation products of bisulphite ions at varying pH levels. Although the

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test organism showed some intrinsic mechanisms to maintain or regulate the intracellular and extracellular pH levels, extremely low pH conditions did not allow growth of the organism, and at the same time, acid conditions seem to have favoured the dissociation of bisulphite and nitrite ions. Such explanations are evident from the general lowering of growth, pigment contents, mineral uptake (NO_3^-, PO_4^{3-} and H_4^+), N_2-fixation, and synthesis of storage product (glycogen). The very obvious enhancement of general growth or other metabolic events at extremely low bisulphite levels could suggest for the possible utilization of bisulphite ions as the sulphur source. The interactions experiments revealed that in natural habitats, the test alga or the blue-greens in general, might be exposed to a multipollutant environment, and the interactions depended on their availability and the prevailing pH conditions, the latter regulating the bioavailability of a particular pollutant.

ECOLOGICAL INVESTIGATION OF A TROPICAL LAKE

Ram Pratap Singh Sup. *Dr. R. S. Ambasht*

Surha Tal, largest in the Ballia district, is an Ox-bow type of perennial fresh water lake formed due to river meandering. It is connected with river Ganga by the stream having bidirectional flow of water depending upon the water level of the river Ganga. The lake is shallow, fertile with phytoplanktons and macrophytes in abundance, and presents a special type of habitat combining fishery and paddy cultivation. It is rich in flora, fish and avian fauna and has a lot of scope for optimal resources utilization by rational planning and management.

The physico-chemical conditions were studied at ten sampling stations distributed over the entire lake and covering littoral and pelagic areas. The field data from June 1977 to May 1978 has been incorporated in the present investigation and the observations have been discussed in the light of existing literature.

The water temperature of littoral was usually higher than pelagic region. It fluctuated between a range of 30.6°C to 16.5°C and 30.1°C to 17.6°C in littoral and pelagic regions, respectively. The temperature records at different depths for June 1977 indicated existence of a diurnal thermal stratification of temperature with a daily circulation.

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The average depths in littoral and pelagic regions of the lake were noted between 112 cm to 280 cm and 213 cm to 482 cm, respectively.

Transparency was maximum in the month of March (172 cm) in littoral and in the month of January (140 cm) in pelagic region. However, the corresponding minimum values were 16 cm in August and 14 cm in May, respectively.

Total, dissolved and suspended solids in the lake water ranged between 27 to 113 ppm, 12 to 72 ppm and 9 to 48 ppm in both the regions of the lake.

The pH of lake water ranged between 8.3 to 10.1. It showed an inverse relationship with carbondioxide and close relationship with the dissolved oxygen of the lake water.

The oxygen concentration of the lake varied within a range of 6.6 ppm to 13.6 ppm with a bimodel pattern of maxima in both littoral and pelagic regions.

The range of free carbon dioxide were 38.5, to 98.9 ppm which attained maximum in August and minimum in February in both the regions.

The values of total alkalinity, carbonate alkalinity and bicarbonate alkalinity ranged between 81.4 to 139.6 ppm, 14.2 to 32.5 ppm and 75.9 to 124.7 ppm, respectively.

The ranges of nitrate and total nitrogen in the lake were 0.14 to 0.99 ppm and 0.82 to 2.95 ppm, respectively.

The calcium and phosphate in the lake water ranged between 25.2 to 84.3 ppm and 0.05 to 0.19 ppm, respectively.

The values of total nitrogen, available phosphorus and calcium in the lake mud varied within the ranges of 1.32 to 4.34, 0.18 to 1.21 and 2.97 to 5.69 mg/g dry mud, respectively.

These attributes vary from month to month as well as in littoral and pelagic regions. The high nutrient loading and ranges of physico-chemical characteristics indicate the eutrophic nature of the lake. However, on the whole the variations in alkalinity, pH etc. do not seem to be affected much either by oxygen or carbon dioxide content of water indicating effective buffering capacity of water which prevents large fluctuations.

Thirty six species of macorphytes were documented in the lake during the study period. The maximum species were recorded in rainy season followed by winter and summer seasons.

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Five life forms have been recognized. Seven species of emergent, eight species of floating leaved, six species of free floating, nine species of submerged and nine species of marshy life forms were recorded. However, a few species exhibited more than one type of life form habit under different habitat conditions.

There were marked seasonal change in species composition, percentage cover of macrophytes and their distributional behaviour. The vegetation indicated 'mature' nature of communities. Free-floating and submerged aquatics were dominant except when cultivated paddy monocultures add significantly to percentage cover of emergent macrophytes. Floating leaved life form was restricted to a few pockets and marshy vegetation also exhibited within a narrow belt.

The values of phytoplankton primary productivity ranged between 162.87 to 846.58 mgC/m^2/day and 281.31 to 998.57 mgC/m^2/day for rates of net and gross production, respectively. The productivity of phytoplankton was always higher in littoral than that of pelagic region. Two distinct peaks in the months of November and May were noted.

The ratio of net and gross production ranged within 0.91 to 0.54 and 0.88 to 0.58 in littoral and pelagic regions, respectively.

The naturally eutrophic nature of lake is supported by the status of phytoplankton primary production status.

Mean standing crop biomass of *Eichhornia crassipes*, the dominant macrophyte of littoral region, was maximum (908.43 g/m^2) in the month of November and minimum (459.44 g/m^2) in the month of April. 'Other species' of this region washhaving maximum standing crop biomass in the month of June (32.08 g/m^2) and minimum in the month of January (162.39 g/m^2). However, total community recorded a maximum of 1340.46 g/m^2 in September and minimum of 809.49 g/m^2 in February.

In pelagic region *Hydrilla verticillata* was having peak standing crop biomass in December (811.98 g/m^2) and minimum in June (502.45 g/m^2). 'Other species' also attained maximum (591.93 g/m^2) in December but minimum (183.09 g/m^2) was noted in May. However, total community followed the trend of dominant species in the region.

Eichhornia crassipes and *Hydrilla verticillata* shared most of the standing crop biomass to the total macrophytic biomass in littoral and pelagic regions, respectively. An inverse relationship between percentage contribution to total biomass for dominant and 'Other species' was eventually noted.

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The values of net productivity in littoral region were maximum (7.24 g/m²/day) for total vegetation in the month of March and minimum of (1.48 g/m²/day) in the month of May. In the months of July, October, November, December, January, February and April a negative production was noted.

In pelagic region macrophytes showed a maximum net production rate in the month of November (5.20 g/m²/day) and minimum in the month of August (0.99 g/m²/day). However, no positive gain was recorded from January to May.

The annual net production was 696.97 g/m²/yr in pelagic region and 609.25 g/m²/yr in littoral region for entire community. The annual net production of dominant and 'Other species' were 443.54 g/m²/yr and 550.36 g/m²/yr in littoral and 354.29 g/m²/yr and 368.56 g/m²/yr in pelagic region, respectively.

The average daily rate of production of entire community was 1.67 g/m²/day and 1.90 g/m²/day in littoral and pelagic regions, respectively. However, dominant and 'Other species' recorded average daily rate of production of 1.22 and 1.51 g/m²/day in the littoral and 0.97 and 1.00 g/m²/day in the pelagic region, respectively.

Turnover values were found maximum of 0.75 and 0.62 for 'Other species' in littoral and pelagic regions, respectively. Dominant species and entire community, however, recorded turnover value of 0.49 and 0.45 in littoral and 0.44 and 0.50in pelagic regions, respectively.

The maximum value of standing crop biomass of *Oryza sativa*—cultivated deep water rice—was recorded 2017.32 g/m² at 20 week age. The rate of net production was maximum at 14 week age (25.67 g/m²/day) and minimum of (0.33 g/m²/day) at 2 week age.

In *Oryza sativa* study of productive structures show that photosynthetic biomass and chlorophyll were concentrated at different levels in response to varying depth of water. On the basis of shape of productive structure (photosynthetic) biomass and chlorophyll three types of profile structures have been identified from shallow to deep water. In one meter deep water rice plant exhibited a profile structure of a shape of spade and had been designated as 'shade' type. In two meter deep water it exhibited a profile structure of a shape of drum, therefore, being called as 'drum' type and in 2.8-3.00 meter deep the profile structure had a shape of spinning top and has been named 'Spinning top' type.

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Light profile studies under paddy at different depths indicate that in low water depths 50% (surface light has been taken as 100%) reaches upto 60 cm and 25% upto 30 cm from the bottom. While in case of mid and deep water fields light intensity of 25% was recorded at 110 cm and 150 cm, respectively from the bottom.

In all cases the maximum green biomass and chlorophyll are concentrated in the depth receiving around 50% of the surface light intensity which probably is optimum for the productivity of 'floating' or deep water rice.

Primary production in terms of energy fixation (K cal/m^2/day) followed the same trend of variation as in the carbon fixation rates for phytoplankton production.

Mean caloric values of all macrophytes were always higher in winter season followed by rainy and summer seasons. The caloric values on dry weight basis varied from 2.96 to 3.69 K cal/g in *Eichhornia crassipes* and 3.38 K cal/g to 3.91 K cal/g in 'Other species' of littoral region.

The mean caloric values on dry weight basis fluctuated from 3.30 to 3.69 K cal/g in *Hydrilla verticillata* and 3.16 to 3.69 K cal/g in 'Other species' of pelagic zone.

The caloric values on ash-free dry weight were obviously higher than that on the total dry weight basis.

In *Oryza sativa* caloric values on dry weight basis fluctuated from 3.69 to 4.11 K cal/g dry weight at 2 week and 20 week age, respectively.

The standing crop of energy for macrophytes and paddy followed the same trend as that of biomass standing crop.

Energy conserving efficiency of autotrophs in litteral were always higher than that of pelagic region. The average annual energy conserving efficiency of phytoplankton was 0.29% in the littoral and 0.24% in the pelagic region.

Oryza sativa was having an average energy conserving efficiency of 3.76% with a maximum of 6.52% and minimum of 0 07%.

In littoral region maximum energy conserving efficiency of *Eichhornia crassipes* was having maximum (1.16%) and minimum (0.07%) in March and May, respectively. However, the total macrophytic community was having an energy conserving efficiency value from 0.12% to 1.09% in October and March, respectively.

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In pelagic region energy conserving efficiency values varied from 0.05% to 0.97%, 0.10% to 0.94% and 0.15% to 1.71% for *Hydrilla verticillata*, 'Other species' and total community, respectively.

However, the average annual energy conserving efficiency of macrophytes was 0.28% and 0.64% in littoral and pelagic regions, respectively.

The maximum annual energy capture was observed for *Oryza sativa* (8291.37 K cal/m^2) followed by macrophytes of pelagic region (3501.78 K cal/m^2), phytoplankton in littoral region (1586.74 K cal/m^2), macrophytes in littoral region (1532.03 K cal/m^2) and phytoplankton in pelagic region (1313.17 K cal/m^2).

As the lake is shallow, macrophytic pathway is more efficient and most of energy flow at primary producer level is through macrophytes and cultivated rice than that of phytoplankton.

POLLUTION PHYCOLOGY OF THE VARANASI FRONTAGE OF RIVER GANGES

Divya Tiwari Sup. *Dr. H. D. Kumar*

A two-year survey of the Varanasi frontage of the river Ganges at various sites near important out falls was conducted to have an idea about the changes in the water quality and its effect on the biological community under increased pollutional stress. Investigations have revealed an adverse effect of the increased pollution which reduces the total number of algal genera to 67 and species to 133 only when compared with some earlier records on the river Ganges at Varanasi as reported by Laxminarayana (1965) and Tripathi (1982).

Major components of the phytoplankton were Diatoms, Green algae and Blue-Green algae. There was total absence of phyto-plankton at the convergence of the Nalla and the river at the heavily polluted site R. Only a few species viz., *Oscillatoria sancta*, *Spirulina major*, *Chlorella vulgaris*, *Scenedesmus bijuga*, *Nitzschia palea*, *Pandorina norum* and Euglenoids at the next down-stream stie R_1. Diversity was found low ($^{-}d = 1.1$) at polluted sites and increased gradually with increasing dilution ($^{-}d = 5.13$) in the concentration of pollutants down stream. The maximum diversity ($^{-}d > 5.0$) occurred at Downstream site for away from the city reach where sufficient dilution of the pollutants had occurred.

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At polluted sites G (1981-82), A, R and R_1, a higher concentration of pollutants was found which was slightly diluted to some extent due to dilution at next downstream sites G_1, A_1 and D.S. A considerable decrease in the concentration of pollutants was found at site G and G_1 in the year in 1982-83 when the factory was closed. During 1981-82 slte G was one of the heavily polluted sites of the river Ganges but during next year much improved conditions were recorded at this site because of closure of the factory. In 1981-82, the factory effluent discharged into the Ganges was found responsible for the very low dissolved oxygen concentration, high B. O. D. and C. O. D. values. Mortality of the fishes occurred by choking of their gills by suspended solids. Low dissolved oxygen concentration was also responsible for their death and very often dead fishes found floating on the surface of water.

A comparative study of the present data with that of the previous investigations by Laxminarayana (1965) and Tripathi (1982) revealed an increased level of pollution by a factor of 2 to 6 times in general. An increase in the value of hardness, chloride, dissolved silica, ammonia nitrogen, nitrate nitrogen, and phosphate was recorded. However, the dissolved oxygen concentration was occasionally found to be nit at the heavily polluted sites G, R and R_1. Chemical oxygen demand (C. O. D.) and Biochemical oxygen demand (B. O. D.) were very high at polluted sites. The above observations point to the grossly polluted nature of the Ganges water.

As the Ganges water is directly used as potable water, an attempt was made to assess its water quality in view of the available drinking water quality standards prescribed by national (Indian Council of Medical Research, 1962) and international organizations World Health Organization, 1971, United States Public Health Service 1962, Environmental Protection Agency 1972 and Royal Commission, 1912. In most of the cases the actual values were higher than prescribed permissive levels of their respective concentrations (total solids, total hardness, calcium, sodium, iron, ammonia etc.) and in some cases the values exceeded even the excessive limits (e. g. calcium, total hardness iron etc.). Dissolved oxygen was always found below the saturation level at all sites and occasionally temporary anaerobic conditions were also recorded. B. O. D. values at all sites were higher than those prescribed for river water by Royal Commission 1865 (2.0 mg^{-1}).

River sediment was found rich in nutrients and showed a high rate of oxygen consumption at polluted sites. A good correlation was found between certain selected parameters. Cultivation of *Chlorella vulgaris* in the sediment extract of the Ganges revealed the presence of both NO_3^-

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and PO_4^{-3}, the major nutrients responsible for plant growth and for eutrophication problems, if present in excess.

Algal bioassay experiments conducted on sewage effluent of site R using *Chlorella vulgaris* and *Scenedesmus bijuga* revealed their high efficiency of nutrient removal from sewage (i. e. from 1 : 1 sewage supplemented medium). Rapid uptake of the nutrients was found by the test organisms, causing 83 per cent to cent-percent removal by the fourth day in case of phosphate and ammonia nitrogen and 49 per cent removal of nitrate nitrogen by fourth day. Bioassay experiment further revealed higher protein and carbohydrate contents of the algae grown in sewage supplemented medium (1 : 1) as compared to those grown in normal Chu 10 medium. These findings show that these forms can serve a dual purpose of purifying the sewage by nutrient removal and possibly as a rich source of nutritional supplement for animals.

Self-purification capacity at heavily sewage polluted stretch R was computed. The deoxygenation constant K_1 was found to be 0.35 and reaeration constant K_2 was found to be 0.969. Self-purification of calculated on the basis of these factors was 2.76—indicating that the river has moderate rate of self-purification due to its slow movement at the site. Allowable loading works out to be 11.86 mg^{-1} and allowable average B. O. D. of the waste water that can be discharged into the river was found to be 54.77 mg^{-1}—indicating a need for sufficient silution (approximately more than 50 per cent) and treatment of the waste water before its discharge into the river. At present the main pumping station at Konia is not working due to which untreated sewage is being discharged into the river Ganges through the main sewer outlet at Raj-Ghat (site R). It is necessary that the sewage should be trapped and treated before its discharge into the river. The sewage should be pumped to some sewage farms before coming into the river; this will minimize the pollution to a great extent. Sewage and waste treatment in treatment plants can also reduce the concentration of pollutants to a great extent which can, then, be discharged into the river without much harm.

The present investigation reveals a higher degree of pollution of the Ganges than the previously recorded values at Varanasi. It is essential to take urgent steps to protect the holy river from further pollution at Varanasi in order to protect the ghats from continuing damage and to save the health of millions of devotees who take bath into the river and drink its raw water.

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EFFECTS OF MUTAGENIC CHEMICALS ON NITROGEN FIXING CYANOBACTERIA

Anil Kumar Tripathi Sup. *Dr. H. D. Kumar*

Heterocystous filamentous strains of *Nostoc linkia*, *Nostoc* sp., and *Anabaena* sp., were isolated from local paddy fields and grown in axenic cultures.

Certain mutagens to induce frameshift mutations affected both nitrogen-fixation and photosynthesis in these cyanobacteria. Low concentrations of acridine orange, ethidium bromide, proflavine and mitomycin C increased heterocyst frequency. Nitrogenase activity was severely inhibited by proflavine but was least affected by ethidium bromide. Increasing concentrations of acridine orange decreased chlorophyll a and phycocyanin contents. Mg^{++} ions partially relieved the toxicity induced by ethidium bromide, acridine orange and proflavine. The toxicity of these photodegradable mutagens was found to be increased under chemoheterotrophic growth as compared to phototrophic growth. The chemoheterotrophic growth with and without nitrate was relatively poor than photoautotrophic growth.

Out of several drugs tested *Nostoc* sp. was most sensitive to streptomycin and p-fluorophenylalanine but quite tolerant to imidazole and polymixin B. Ethidium bromide, acridine orange, proflavine and mitomycin C caused pronounced lethal effects but were weakly mutagenic. Nitrosoguanidine (MNNG) proved to be a potent mutagen in these cyanobacteria as it induced mutations at high frequency and was not very lethal.

5—Fluorotryptophan adversely affected growth and heterocyst formation in *Nostoc linkia*. Employing nitrosoguanidine mutagenesis, fourteen mutant clones of *Nostoc linkia* resistant to 5-fluorotryptophan were isolated and characterized with respect to heterocyst frequency and pigment content. In general, the mutants showed higher pigment content and lower heterocyst frequency in 5-fluorotryptophan supplemented culture medium, suggesting that the mutants might have acquired an ability to metabolize 5-fluorotryptophan and to use tryptophan moiety as a nitrogen source.

Metronidazole, an inhibitor of ferredoxin-linked reductases, inhibited nitrate reductase and glutamine synthetase activity of wild-type *Nostoc* sp. Metronidazole-induced toxicity was partially relieved by NH_4^+ (1 mM) supplementation. Metronidazole selection of nitrosoguanidine-induced

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pigment mutants produced a brown coloured phenotype. This mutant exhibited reduced levels of chlorophyll a and carotenoised, absence of phycocyanins, production of chains of heterocysts and slow growth rate in minimal medium. This mutant imparted a slightly brownish colour to the medium and was to found to secrete hydroxyproline extracellularly. Mutants which overproduce proline or related substances may possibly prove useful if they show greater tolerance to increased drought or salinity stress (Valentine, 1982).

In order to study the mode of action of some mutagens, uptake studies revealed a relatively efficient mode of acridine orange uptake in *Nostoc* sp. Spectral changes in the absorption spectra, caused by the binding of intercalating mutagens to cyanobacterial DNA *in vitro* revealed that most probably only electrostatic attractions operate in the mutagen-DNA binding. My studies on mutagen-DNA binding *in vitro* suggest that if the same level of binding observed *in vitro* also occurred *in vivo* then due to the relatively weaker intercalation binding there is lesser possibility of mutation induction by these mutagens. Ethidium bromide, acridine orange and mitomycin C confer stability to DNA towards thermal denaturation. It appears that mitomycin C binds to DNA by crosslinking and requires Mg++ ions for more efficient binding. Poor intercalation may not be able to induce frameshift mutations but can interfere with replication and/or transcription of DNA in the cells.

Long term exposure of *Nostoc* sp. to sublethal concentrations of acridine orange produced two variant phenotypes (acridine dyes are known to cure plasmids in bacteria). Both the variants were non-heterocystous and sensitive to polymixin B. Cyanobacterial plasmids are so far known to be cryptic. To check whether these phenotypic changes in the variants are plasmid-borne, agarose gel electrophoresis of wild and variant types of *Nostoc* sp. was done. Wild type showed presence of three distinct plasmid bands whereas variant type showed none. Simultaneous loss of heterocyst formation and polymixin B tolerance in *Nostoc* sp. indicates that probably these traits may be carried on plasmid. Production of nitrogen fixing, non-heterocystous derivative of $Het^{-}PmB^{s}$ strain suggests some other possibilities which I have discussed in this thesis alongwith a tentative model.

A comparison of Hind III DNA fragments with *Nostoc linkia* plasmid DNAs, on agarose gels revealed that *Nostoc linkia* plasmids are of low molecular weight and may possibly be used to construct a suitable cloning vehicle. Although, gene transfer in mixed cultures had been achieved in some heterocystous cyanobacteria, categorical demonstration

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of transformation is lacking. I have chemically extracted DNA from propionate and amitrol resistant mutants of *Nostoc linkia*, developed competence by means of $CaCl_2$ treatment and achieved polyethylene glycol mediated DNA uptake by recipients at a frequency of 1.91 precent in *Nostoc linkia* and 0.48 percent in *Nostoc* sp. This frequency of transformation is quite high.

The more noteworty contributions made in the present research are : i) Understanding the *in vitro* interactions of certain mutagens with DNA; ii) demonstration of small plasmids, and iii) development of a fairly efficient and suitable transformation protocol. These achievements point to some potential scope of *in vitra* mutagenesis and genetic engineering in the nitrogen-fixing cyanobacteria used in this study.

SOIL SALINITY AND REPRODUCTIVE BEHAVIOUR OF DACTYLOCTENIUM AEGYPTIUM (LINN.) BEAUV

Umesh Kumar Varshney Sup. *Dr. G. N. Chaudhuri*

The thesis embodies two sections. Section 'A' adumbrates ecology of salt-affected habitats embracing observations on climate, soil and vegetation. Section 'B' adumbrates results of investigations with plaussible interpretations pertaining to the reproductive behaviour in response to soil salinity of *Dactyloctenium aegyptium* (Linn.) Beauv., a facultative halophyte, commonly occurring in the grass covers of the Indo Gangetic plains of the Indian sub-continent. Assessment of the response of populations from non-saline and saline habitats to various ions which usually contribute to soil salinity and alkalinity with respect to germination, growth and reproductive capacity with an appraisal of population differentiation has been the theme of the thesis.

The study sites presented a barren physiognomy with scattered patches of vegetation of low species diversity inter-spersed with openings of variable dimensions.

The edaphic environments of salt-affected sites under present study were characterized by high salt content; high pH, high exchangeable sodium percentage (ESP), low organic matter and low nitrogen contents round the year with some rhithmic seasonal variations. Capillary rise coupled with evaporation resulted in surface accumulation of salts. High

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nitrogen together with a warm and humid conditions was responsible for an enhanced microbial activity in these habitats resulting a low C/N in the rainy season.

Vegetal growth was optimum and species diversity was maximum during rainy season. Plant communities attained a simplified structure in summer season due to increased total soil moisture stress and were represented by a few species with halophytic potential. *Sporobolus marginatus* was the dominant grass round the year. *Cynodon dactylon*, *Dactyloctenium aegyptium*, *Eragrostis tenella*, *Phyla nodiflora* and *Desmostachya bipinnata* were considered co-dominants.

Pattern of distribution of individuals of all species was **'contagious.'** The degree of contagion varied from species to species and from season to season within a species. Patchiness in vegetation at study sites increased from rainy to summer season due to successive degeneration and drying off of the individuals of various species and appearance of large barren spots due to elimination of ephimerals subsequent to rainy season on account of increasing salt-stress in the edaphic environment. Whereas clumping in different species, when observed individually, was high during the rainy season due to gregariousness of individuals in case of annuals and extensive vegetative propagation in case of perennials at areas of low salinity. High degree of clumping in species such as *Dactyloctenium aegyptium* and *Eragrostis tenella* was due to enormous production of heavy seeds with ill-equipped dispersal mechanism resulting a restricted despersal close to the parents. Clumping in *Cynodon dactylon*, *Desmostachya bipinnata*, *Dichanthium annulatum*, *Phyla nodiflora* and *Sporobolus marginatus* was ascribable to their inherent capability of rapid vegetative spread.

Occurrence of *Dactyloctenium aegyptium* both in normal as well as in salt-affected habitats during rainy season indicated a halophytic potential in the species. Capability of the species to get over with the extremes of salt-affected habitats through phenological and physiological adaptations and by completing its life-cycle a month earlier than what was normally observed in nonsaline (normal) habitats indicated existence of an adaptation to gradual build up of salinity stress in the edaphic environment subsequent to rainy season.

Relatively better seed germination of saline population under all ionic treatments and also in controls and better establishment of seedlings subsequent to germination in Na^-, Cl^-, HCO_3^-, CO_3^{2-} and SO_4^{2-} treatments reflected an adaptation in saline population for successful ecesis in specialized habitats dominated by these salts.

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Differential growth behaviour of non-saline and saline populations in fields, in controls and under various ionic treatments also revealed presence of genetically fixed differences between the populations. Consistently lower biomass and higher shoot/root ratio of plants of saline population in their natural habitat as well as in controls and in various ionic treatments indicated an eco-physiological differentiation between the saline and non-saline populations.

Production of relatively heavier, bigger and darker brown seeds by saline population both in its natural habitat as well as in untreated garden loam and also in various ionic treatments reflected a heritable adaptation in plants of this population occupying the local salt-affected habitats where germination and establishment call for a better insurance in the face of relatively shorter water regime normally associated with such habitats. Seeds of saline population, because of being heavy, are seldom dispersed beyond the vicinity of their parents, and with the result the population remains confined to these specialized habitats with patchy distribution.

Higher reproductive capacity of saline population both in the field as well as in experimental studies with various dosimetry treatments of ions, reflected a salinity induced preadaptation in a section of the species which made it genetically better equipped to ecise and flourish in salt-affected habitats characterized by Na^+, HCO_3^-, CO_3^{2-} and Cl^-.

Capability of saline population to stand higher Na^+ levels where non-saline population succumbed and more susceptibility of the latter to HCO_3^-, CO_3^{2-}, SO_4^{2-} and Cl^- in the edaphic environment revealed a **'halo-ecotypic differentiation'** within the species. The differentiation was pin-pointed to be due to Na^+ ions in the edaphic environment of local salt-affected areas due to precipitation of Ca^{2+} and Mg^{2+} as insoluble carbonates at higher pH.

In conclusion, it may be said that a section of *Dactyloctenium aegyptium* (Linn,) Beauv., occuring in normal non-saline habitats in the Indo Gangetic plains might have seggregated into salt-adapted biotypes in response to the excessive accumulation of Na^+ dominated water soluble salts in the edaphic environment which subsequently survived natural selection and maintained existence as a **'halo-ecotype'.**

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CHEMISTRY

SYNTHETIC, STRUCTURAL AND BIOLOGICAL STUDIES ON SOME 3D-METAL COMPLEXES OF 2—FURANTHIOCARBOXY HYDRAZIDE AND ITS N¹-SUBSTITUTED DERIVATIVES

Seema Agrawal Sup. *Dr. N. K. Singh*

Since long back transition metal complexes of sulphur containing ligands have been of great interest because of their (i) variable stereochemical behaviour, (ii) significant biological activity and numerous commercial uses. In comparison to the extensive studies made on the ligational behaviour of hydrazides having oxygen and nitrogen as donor atoms towards transition metal ions, the complex chemistry of thiohydrazide is very limited. Only recently few papers have appeared on transition metal complexes of thiohydrazides such as thiobenzhydrazide and thioacethydrazides. Further, the ligational behaviour of thiohydrazides has been found to be different from hydrazides in following respects; (i) since thiocarboxy group is a better π-acceptor, sulphur donor ligands form more stable complexes with soft or class *b* metal ions than oxygen donor ligands and this is due to the formation of stronger meta ligand bonding (ii) sulphur differs from oxygen in having a better tendency for thioenolization, if there is at least one hydrogen atom adjacent to the C=S bond leading to the formation of deprotonated complexes easily with thiohydrazides than hydrazides.

Transition metal complexes of thiosemicarbazides, thiosemicarbazones and dithiocarbazates have shown a wide spectrum of biological activity such as antifungal, antiviral, antibacterial and antineoplastic activities. Recently, some Cu(II), Zn(II) and Fe(II) complexes of substituted *bis*-thiosemicarbazones and α-N-heterocyclic carboxaldehyde thiosemicarbazanes have been found to possess very remarkable anticancer activity against a variety of tumors. Some workers have studied the mechanism of action of these complexes and concluded that NNS donor group is responsible for carcinostatic activity. Since thiohydrazides too have NNS donor group, it might be expected that their 3d-metal complexes should also possess these activities and in fact some of our compounds showed very significant antifungal, antibacterial and anticancer activities.

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Synthesis of the Ligands

2-Furanthiocarboxyhydrazide (Hfth) was prepared as reported in the literature by the reaction of furfural with ammonium polysulphide, acidifying the resulting ammonium salt of dithioacid with HCl and treating it with $N_2H_4.H_2O$. Salicylaldehyde-2-furanthiocarboxyhydrazone (H_2L) was obtained by the condensation of Hfth with salicylaldehyde. N,N'-*bis*-(2-furanthiocarbonyl hydrazine) (H_2dfth), N'-2-furancarbonyl-N^2-2-furanthiocarbonyl hydrazine (H_2cfth) and N-salicyl-N'-2-furanthiocarboxy hydrazine (H_2sfth) were prepared by mixing the sodium hydroxide solutions of carboxymethyl-2-furandithioate and Hfth, 2-furoic acid hydrazide and salicyl hydrazide, respectively, in 1:1 molar ratio and adding dil. acetic acid to the above reaction mixture after standing it for~2 hr at room temperature. The ligands thus synthesized were suction filtered, washed with H_2O and/or ethanol, dried *in vacuo* and recrystallized from hot ethanol (except H_2dfth). The ligands were characterized by C, H, N and S analyses, m. p. and IR, NMR and electronic spectral studies.

Preparation of the Complexes

The addition and cationic-anionic complexes were prepared by reacting the alcoholic solutions of the appropriate metal chloride and the ligand in 1:2 molar ratio. In case of $[Co(Hfth)_3]Cl_3$, $[Ni(H_2L)_2Cl_2]$ and $[Cu(H_2L)Cl_2]$ few drops of dil. HCl were added. Deprotonated complexes were obtained by mixing the aqueous/alcoholic solutions of the appropriate metal salt and the ligand in presence of CH_3COONa/KOH and digesting the above reaction mixture on water bath for 30 minutes. Attempts to prepare the hydrazones by the condensation of Hfth and pyridine-2-and-4-carboxaldehydes were not successful, therefore, $M(pfth)_2$, M(Ifth), Cu(Ifth) and $Co(Ifth)_3$ were obtained by refluxing the ethanolic suspension/DMSO solution of the respective $M(fth)_2$ and an excess solution of pyridine-2-or-4-carboxaldehyde for about~3 hr. All the complexes, thus obtained were suction filtered, washed with H_2O, ethanol or methanol and dried *in vacuo*. the complexes were analysed for their metal, nitrogen, sulphur, chloride and water contents.

Results and Discussion

Generally, the complexes are insoluble in water, some of them are soluble in EtOH and MeOH, and except few all are soluble in DMF and DMSO. The molar conductance values of all the soluble complexes at 10^{-3} M concentration in MeOH/DMF (~40, ~20) demonstrate their

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non-ionic nature except [VO(Hfth) Cl]$_2$Cl (80.0 in MeOH), [Cr(Hfth)$_2$ Cl$_2$] Cl.H_2O (70.5 in DMF); [Ni (Hfth)$_3$]Cl_2 (134.15 in DMF) and Co (Hfth)$_3$ Cl_3 (240.6 in MeOH) which are ionic being 1 : 1, 1 : 2 and 1 : 3 electrolytes, respectively.

Magnetic Moment

The magnetic moments of VO (IV) (160-1.79 B. M.) and Cu (II) (1.67-2.05) complexes correspond to the presence of one unpaired electron. The magnetic moment values for Cr (III) complexes lying in the range 3.9-4.1 B. M.; Mn (II) complexes in the range 5.6-6.2 B. M. and Fe (II) complexes (4.9 B. M.) are normal corresponding to the presence of three, five and four unpaired electrons, respectively, suggesting them to be high-spin octahedral.

Electronic Spectra

The spectra of all the VO (IV) complexes display two bands in 10260-13330 and 16390-17390 cm^{-1} regions assigned to $^2B_2 \rightarrow {}^2Eg$ and $\rightarrow {}^2B_1$ transitions, respectively, in octahedral geometry of the complexes. The spectrum of VO (sfth). H_2O, however, shows the bands at 17390 and 25000 cm^{-1} assignable to $^2B_2 \rightarrow {}^2B_1$ and $^2A_1$ transitions, respectively, on the basis of the above geometry.

Photoacoustic Spectra

Photoacoustic spectroscopy is an important tool for studying complexes where the light absorbed by a solid sample is detected as an acoustic signal. The structures of the complexes have been assigned on the basis observed d-d transitions in their photoacoustic spectra. The bands at 480 and 760 nm in the photoacoustic spectra of Co (Ifth)$_3$ further supports its octahedral geometry.

ESR Spectra

VO(L).2H_2O, VO(sfth).H_2O, Cu(H_2L)Cl_2, CuL.H_2O, Cu(sfth) and Cu(HL)$_2$ display isotropic e. s. r. spectra at room temperature and nearly axially symmetric at L. N. T. The signals in the R. T. spectra further show extra hyperfine lines (not very prominent in VO(sfth).H_2O) consistent with the interaction of the unpaired electron of the Cu(II) ion with one ^{14}N nucleus in case of Cu(H_2L)Cl_2 and two ^{14}N nucleus in the case of VO(sfth).H_2O, Cu(sfth) and Cu(HL)$_2$. These hyperfine lines are very distinct in 77 K spectra of the complexes (except VO(sfth).H_2O) further reinforcing one or two nitrogen coordination with the metal ion. The calculated g values indicate that the ground state in VO(IV) and Cu(II) is d_{xy} and $d_{x^2-y^2}$, respectively.

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Mössbauer Spectra

The Mössbauer spectral studies on Fe(sfth).$2H_2O$ and Fe(pfth)$_2$ show the isomer shift values of 0.69 and 0.50 mm sec^{-1} and quadurpole splittings of 1.10 and 0.40 mm sec^{-1}, respectively, further supporting their high and low-spin octahedral geometries, respectively. The non-zero quadurpole splitting is indicative of some distortion in the octahedra owing to non-identical donor atoms.

IR Spectra

The IR spectra of all the ligands display bands at 3350 and 880 cm^{-1} due to ν (NH) and ν (C=S) modes, respectively. Additional bands at 3180 and 3140 in the case of Hfth may be attributed to ν (NH) of primary amine group and those at~3100 cm^{-1} in the case of H_2L and H_2sfth to ν (OH). The bands due to ν (OH) in case of H_2L and ν (NH) of secondary amine group in case of Hfth remain practically unchanged in the spectra of the adducts/cationic anionic complexes whereas the bands due to ν (NH) of the primary amine group ν (C=N) and ν (C=S) suffer negative shifts of 30-50 cm^{-1} indicating coordination through terminal nitrogen and thione sulphur in Hfth complexes and azomethine nitrogen and thione sulphur in H_2L complexes.

^{1}H NMR Spectra

The ^{1}H NMR spectrum of H_2L exhibits the —CH=N, —OH(br) and NH+ ring proton signals at δ 8.90, δ11.23—11.56 and δ6.66—8.33 ppm, respectively. Absence of phenolic proton and presence of —NH proton signal in the spectrum of Zn(HL)$_3$, is suggestive of the monobasic nature of the ligand. The spectrum of ZnL.C_2H_5OH does not show the signals due to both —NH and —OH protons indicating dinegative tridentate behaviour of the ligand. Furthermore, the spectrum of this complex displays a triplet at δ 1.08 ppm due to —CH_3 protons and a quartet at δ 3.41 ppm due to —CH_2—protons indicating the presence of coordinated ethanol molecule in the complex.

Antimicrobial Activity

Antifungal activity

As expected for the compounds containing >N—C=S moiety, the ligands and their Mn(II), Co(II) and Cu(II) complexes are highly fungitoxic at all the three concentrations studied but the maximum has been observed at the highest concentration i. e. 10000 ppm. As expected the complexation generally increases the biological properties of the ligands and the complexes are found to be more potent bactericides and fungi-

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cides than their parent ligands. Thus, $Cu(HL)_2$ almost completely inhibits the fungal growth at all the three concentrations. $Mn(HL)_2$ and Co(HL) (L) exhibit a greater fungitoxicity against *R. oryzae* but are less active against *A. niger* at all the three concentrations as compared to H_2L.

Antibacterial activity

Due to the limited solubility of the compounds in DMSO, it has not been possible to screen the activity at higher concentrations. Cu(II) and Zn(II) complexes have weak antimicrobial action as compared to Hfth for which significant inhibitory effect against all the bacteria tested has been observed. All the complexes inhibit the growth of *S. aureus* but towards other bacteria the inhibition is not very pronounced. The growth of *K. pneumoniae* was not checked by H_2sfth, whereas Zn(sfth) and Cu(sfth) inhibited the growth of this bacteria.

Antitumor activity

In vivo antitumor activity of Cu(sfth) has been tested against ascites Dalton's lymphoma and solid fibrosarcoma tumor systems in mice. The following values were obtained for LD_{50} : 45 mg/Kg body wt. of Cu (sfth) for Dalton's lymphoma in Dba and 75 mg/Kg body wt. of Cu(sfth) for fibrosarcoma in mice.

Histological Study

Light microscopic study of the treated tumor mass demonstrated that certain morphological changes occurred in the regression of tumor i. e. the mitotic activity of tumor cells was inhibited soon after the injection of Cu(sfth) and lymphocytes, leucocytes, macrophages appeared within tumor mass after 2-6 days of treatment which shows that the compound act at the cellular level and the regression of tumor is dose dependent.

INVESTIGATIONS IN THE ORGANIC CHEMISTRY OF NITROGEN AND SULPHUR COMPOUNDS AND RELATED SYSTEMS

Mohammad Ramzan Ali Sup. *Dr. V. K. Verma*

The work embodied in this thesis has been divided into two parts. *Part I* incorporates the syntheses of S-Alkyliso-N-arylthiocarbamoyl—arylthioamides, N—arylthiocarbamoyl-arylthioamides, 1,5—disubstituted and 1, 1, 5—trisubstituted-2-S-benzyliso 2, 4—dithiobiurets, 1,5—

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disubstituted and 1, 1, 5—trisubstituted 2, 4—dithiobiurets,and the studies in their oxidative dealkylation and direct oxidation leading to the formation of 5—substituted 3—substitutedimino-1, 2, 4—dithiazoles, 3, 5—disubstitutedimino 1, 2, 4—dithiazolines and dithiazolidines. *Part-II* describes the preparation of S-benzyliso-N-phenylcarbamoyl-arylthioamides, N-phenylcarbamoyl—arylthioamides, 1, 5-disubstituted -2 S-benzyliso-2, 4—thiobiurets, 1, 5—disubstituted-2, 4—thiobiurets with a view to extend the oxidative debenzylation and cyclisation reaction to these systems and to study their conversion into the sulphur and nitrogen heterocyclic compounds e. g. 2, 5—disubstituted-3-oxo-2, 3—dihydro-1, 2, 4—thiadiazoles and corresponding 1, 2, 4—thiadiazolidines.

Part I

Arylthioamides obtained by the thiohydrolysis of corresponding nitriles, were alkylated in presence of sodium methoxide as a catalyst. The resulting S-alkyliso-arylthioamides were subjected to the reaction with appropriate arylisothiocyanate to yield corresponding S-alkyliso-N-arylthiocarbamoyl-arylthioamides. The chloroform/benzene solutions of the latter were treated with bromine, when the alkyl group was eliminated as alkyl bromide followed by ring closure to the related 5-aryl-3-arylimino-1,2,4-dithiazoles. These dithiazoles have also been obtained by the oxidation of the corresponding N-arylthiocarbamoyl-arylthioamides, which were obtained by the reductive dealkylation of the related S-alkyliso-N-arylthiocarbamoyl-arylthioamides with hydrogen sulphide in pyridine-triethylamine and also by reduction of IV under identical conditions. The structural assignments of the compounds, in all the cases, were rationalized by their synthesis through alternative routes, wherever possible, as described above, and also by elemental and spectral analyses.

Later, the synthesis of certain 5-aryl-1, 1-methylphenyl-2-S-benzyliso-2, 4-dithiobiurets was achieved by the interaction of 1, 1-methylphenyl-2-S-benzylisothiourea and appropriate arylisothiocyanate. The isodithiobiurets, on oxidation with molecular bromine in chloroform were found to oxidatively dealkylate and cyclise into the related 3-arylimino-5-(N methylanilino)-1, 2, 4-dithiazolines. These have also been obtained by the direct oxidation of the related 5-aryl-1, 1-methylphenyl-2, 4-dithiobiurets. The compounds were obtained by the reductive debenzylation of the corresponding isodithiobiurets with dry hydrogen sulphide in pyridinetriethylamine medium and also by the

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reduction of the related dithiazolines with ethanolic ammoniacal hydrogen sulphide.

In all the cases, the structure of the compounds and were confirmed by their synthesis through alternative routes as described above, and also by mixed melting points, elemental analyses and identical IR spectra.

The next scheme incorporates the preparation of some 5-aryl-1—(arylideneamino)-2-S-benzyliso-2, 4-dithiobiurets and related 2, 4-dithiobiurets from the related thiosemicarbazone and their oxidation to the corresponding 3, 5-disubstitutedimino-1, 2, 4-dithiazolidines.

The appropriate thiosemicarbazone was benzylated with benzyl chloride in ethanol/methanol in presence of sodium ethoxide/sodium methoxide and the resulting S-benzyliso derivative was condensed with appropriate arylisothiocyanate to afford 5-aryl-1-(arylideneamino) -2-S-benzyliso-2, 4-dithiobiurets. The latter in chloroform solutions were treated with molecular bromine when the benzyl group of these was dislodged as benzyl bromide followed by ring closure to the related 3-arylimino-5-(N-arylidene hydrazono)-1,2, 4-dithiazolidines.

These compounds have also been obtained by the oxidation of the related 5-aryl-1-(arylideno)-2, 4-dithiobiurets which in turn were obtained by the reductive debenzylation of the related isodithiobiurets with hydrogen sulphide in pyridinetriethylamine and also by reduction of with hydrogen sulphide in ethanolic ammoniacal solutions. The structures of the compounds, in all the cases, were substantiated by their synthesis through alternative routes wherever possible, IR and proton NMR spectra.

Next, we turned our attention towards the synthesis of 3-arylimino-5-(N-cyclohexylidene hydrazono)-1, 2, 4-dithiazolidines by the successful oxidative debenzylation and cyclisation of the corresponding 5-aryl-1-(cyclohexylideneamino)-2-S-benzyliso-2, 4-dithiobiurets.

The cyclohexanone thiosemicarbazone was benzylated. The resultant free base of S-benzyliso-cyclohexanonethiosemicarbazone was condensed with the appropriate arylisothiocyanate to yield 5-aryl-1-1-(cyclohexylideneamino)—2—S—benzyliso—2,4-dithiobiurets. Molecular bromine was found to oxidise and cyclise the compounds in chloroform solution to the related 3-arylimino-5-(N-cyclohexylidenehydrazono)-1,2,4-dithiazolidines. The elimination of the benzyl group was evident from the evolution of the lachrymatory fumes of benzyl bromide. The identity of these compounds was confirmed from their preparation by

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the oxidation of the related 5-aryl-1-1-(cyclohexylideneamino)-2,4-dithiobiurets. These compounds were obtained by the reductive debenzylation of the related isodithiobiurets with dry hydrogen sulphide in pyridinetriethylamine and also by reduction of with hydrogen sulphide in ethanolic ammoniacal solution. The structural assignment of the compounds and were achieved by their synthesis through alternative routes, mixture melting points, elemental and spectral analyses.

Part—II

Firstly, it describes the reaction of arylthioamides, obtained by thiohydrolysis of the related arylnitriles, with phenyl isocyanate in presence of a catalyst. The resulting products were identified as N-phenylcarbamoyl-arylthioamides with benzyl chloride afforded the corresponding S-benzyliso-N-phenylcarbamoyl-arylthioamides. The oxidation of the latter with molecular bromine, through oxidative debenzylation and cyclisation afforded the compounds. These compounds which could also be conveniently synthesised by the cyclodehydrogenation of N-phenylcarbamoyl-arylthioamides with bromine. Compounds were also obtained by the reduction of III with hydrogen sulphide in pyridine-triethylamine medium. The structure of the compounds were corroborated by underpressed mixed melting points, superimposable IR spectra and proton NMR spectra.

Secondly, it incorporates attempts to extend the oxidative debenzylation reaction to an allied system. Substituted thiosemicarbozones were benzylated with benzyl chloride in methanol (or ethanol) in presence of sodium methoxide (or ethoxide), and the resulting S-benzyliso-alkyl (or aryl) thiosemicarbazones were condensed with phenyl isocyanate to afford the related 1-alkylidene (or arylidene) amino-5-phenyl-2-S-benzyliso-2,4-thiobiurets. The compounds in chloroform solution were subjected to oxidation with molecular bromine, when benzyl group was knocked off as benzyl bromide followed by ring closure to the related 5-N-alkylidene (or arylidene) hydrazono -3-oxo-2-phenyl-1,2,4-thiadiazolidines. The compounds were also obtained by the oxidation of the related 1-alkylidene (or arylidene) amino -5-phenyl-2, 4-thiobiurets, which in turn were prepared by reductive debenzylation of the related isothiobiurets with hydrogen sulphide in pyridine-triethylamine medium. The structural characteristics of the compounds were substantiated by their synthesis through alternative route wherever possible and also by elemental and spectral studies.

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SYNTHESIS AND STRUCTURAL INVESTIGATIONS OF ACYL HYDRAZINE SCHIFF BASE COMPLEXES WITH SOME TRANSITION AND INNER TRANSITION METAL IONS

Rudra Mani Dubey Sup. *Dr. K. K. Narang*

Chapter I :

After briefly introducing the Schiff base chemistry, hydrazines and hydrazones, a review of some salient features particularly, spectral, stereochemical and magnetic of manganese (II), cobalt (II), nickel (II), copper (II), zinc (II), oxotitanium (IV), oxozirconium (IV), dioxouranium (VI) and thorium (IV) are given in this Chapter.

Chapter II :

Experimental details regarding the preparation of basic materials, the organic acid hydrazides (viz., benzoic, salicylic, anthranilc acid hydrazides and oxalic, malonic and succinic acid dihydrazides) and their salicylaldehyde Schiff bases such as salicylaldimine benzamide (SBH); salicylaldimine salicylamide (SSH) salicylaldimine acetamide (SAcH); salicylaldimine anthranilamide (SAtH); disalicylaldimine oxamide (DSOH); disalicylaldimine malonamide (DSMH); disalicylaldimine succinamide (DSSH) and glyoxal Schiff bases such as glyoxalimine dibenzamide (GDBH); glyoxalimine disalicylamide (GDSH); glyoxalimine oxamide (GDH); glyoxalimine malonamide (GMH) and glyoxalimine succinamide (GSH) are given in this Chapter. Procedures for elemental estimations, the physicochemical techniques and instruments used are also described.

Chapter III :

After briefly reviewing the literature on benzoyl, salicoyl and acetyl hydrazines and their hydrazones, synthesis and physicochemical studies of oxotitanium (IV), oxozirconium (IV), thorium (IV) and dioxouranium (VI) complexes with salicylaldimine benzamide (SBH), —salicylamide (SSH) and —acetamide (SAcH) are described in this Chapter.

The complexes of general compositions, $M(L-H)_2$ (where M = TiO(IV), ZrO(IV), UO_2(VI) and L = SBH, SSH, SAcH); $Th(L-H)_4$ (where L = SBH, SSH and SAcH) and Th $(L—2H)_2$ (where L = SBH and SSH) are reported. Most of the complexes melt with decomposition above 250°C and are insoluble in common organic solvents. Oxotitanium (IV) complexes are partially soluble in chloroform and benzene but their very low conductance values suggest their non-electrolytic nature. On the basis of solubility, decomposition temperature and low molar

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conductance values, polymeric nature of complexes in solid state is suggested.

Chapter IV :

The literature on transition metal complexes of salicylaldimine anthranilamide (SAtH) and disalicylaldimine anthranilamide (DSAtH) has been briefly surveyed. Syntheses of the complexes of the types M(SAtH-H)2; M=TiO(IV), ZrO(IV) and UO_2(VI); M(DSAth-2H); M=TiO(IV), Zro(IV) UO_2(VI); $Th(L\text{-}H)_2$; L = SAtH and DSAtH are discussed.

Chapter V :

After a short introduction and literature survey on the transition and non-transition metal complexes of oxaldihydrazide, malondihydrozide and succindihydrazide the oxotitanium (IV), oxozirconium (IV), thorium (IV) and dioxouranium (VI) complexes of disalicylaldimine oxamide (DSOH), -malonamide (DSMH) and -succinamide (DSSH) are described in this chapter.

Chapter VI :

With a brief introduction and literature on polymeric Schiff bases and their transition and non-transition metal complexes the complexes of manganese (II), cobalt (II), nickel (II), copper (II) and zinc (II) with glyoxalimine dibenzamide (GDBH) and -disalicylamide (GDSH) are described in this chapter.

Chapter VII :

In this chapter oxotitanium (IV), oxozirconium (IV) thorium (IV) and dioxouranium (VI) complexes with glyoxalimine dibenzamide (GDBH) and glyoxalimine disalicylamide (GDSH) are discussed.

Chapter VIII :

After a brief introduction, synthesis and characterization of manganese (II), cobalt (II), nickel (II), copper (II) and zinc (II) complexes with glyoxalimine oxomide (GOH), glyoxalimine malonamide (GMH) and glyoxalimine succinamide (GSH) polymers are described in this chapter.

Chapter IX :

This chapter describes oxotitanium (IV) oxozirconium (IV), thorium (IV) and dioxouranium (VI) complexes with glyoxalimine oxamide (GOH), glyoxalimine malonamide (GMH) and glyoxalimine succinamide (GSH) polymers.

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MONOTHIOCARBAMATE AND MONOTHIOCARBONATE DERIVATIVES OF A FEW TETRA AND PENTAVALENT ELEMENTS

Virendra Kumar Gupta Sup. *Dr. V. D. Gupta*

The broad spectrum of the chemistry of metal complexes derived from sulfur ligands ranges from synthesis to applications in many diverse fields. In the recent years unsymmetrical sulfur ligands and their metal complexes have also been the focal point of interest. These class of compounds are expected to exhibit different bonding patterns of the ligands and other structural features like clustering of sulfur atoms in addition to other properties which are observed in the metal complexes of symmetrical sulfur ligands. This has led us to investigate the chemistry of monothiocarbamate and monothiocarbonate derivatives of a few tetra and pentavalent elements.

During the course of the present investigations a number of new metal derivatives of monothiocarbamate and monothiocarbonate have been isolated and characterized by physicochemical techniques such as molar conductance, molecular weight data and infrared and NMR spectroscopy. With the limited evidence it has not been possible to establish the distributions of the ligand atoms in the suggested structures. The access to ^{119}Sn, ^{13}C and variable temperature ^{1}H NMR could have been more revealing. Unfortunately the facilities are not available in most of our research centres. The ^{13}C NMR spectral data of a compound and priliminary structural data of diphenyltin (IV)— bis (p-tolyl-monothiocarbonates) by X-ray diffraction pattern have been included in the text. The work embodied in the thesis can be summarized under the following heads :

I. Tin (IV) derivatives of N, N-dialkylmonothiocarbamate.

II. Silicon (IV), Germanium (IV), Titanium (IV) and Zirconium (IV) derivatives of N, N-dialkylmonothiocarbamate.

III. Niobium (V) and Tantalum (V) derivatives of N, N-dialkylmonothiocarbamate.

IV. Tin (IV) derivatives of monothiocarbonate.

I. *Tin (IV) Derivatives of N, N-Dialkylmonothiocarbamate* : The complexes of the types $SnX_{4-n}(SOCNR_2)_n$, $R'SnCl_{3-n}(SOCNR_2)_n$, $R''SnCl_{2-n}(SOCNR_2)_n$ and $R_3''Sn(SOCNR_2)$ [X=Cl, Br, I; R=Me, Et; R′=Ph, n-Bu; R″=n-Pr, n-Bu; n=1-4] have been synthesized

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by reacting the stoichiometric amounts of sodium or dialkylammonium salts of N, N-dialkylmonothiocarbamates with the appropriate tin (IV) halides or organotin (IV) chlorides. These were crystallizable solids or liquids and were found to be monomeric in benzene cryoscopically.

The trihalo-, organodichloro-, diorganochlorotin (IV) complexes appear to have essentially 5-coordinate structure as inferred from their infrared and ^{1}H NMR spectral data. Triorganotin (IV) derivatives have been found to be notably different in exhibiting carbonyl absorption at comparatively higher frequency suggesting somewhat weak Sn—O interaction. In them the presence of two absorption due to ν_{as} (Sn-C) and ν_s (Sn-C) vibrations in the far infrared region may be due to the non-planarity of the organo groups bonded to tin.

Dihalo-, organochloro-, and diorganotin (IV) bis (N, N-dialkylmonothiocarbamates) appear to possess octahedral geometry. The complexes of the type Y_2 Sn $(SOCNR_2)_2$ (Y = Cl, n – Pr, n – Bu) may have *cis* structures as indicated by the two absorptions in their far infrared spectra owing to asymmetric and symmetric stretching vibrations assignable to (Sn-Cl) and (Sn-C) in dichloro- and diorganotin (IV) complexes respectively. The ^{1}H NMR spectra of the complexes show a doublet due to Me_2-(N) and overlapping quartets and triplets due to Et_2-(N) protons in their respective complexes perhaps arising from the non-equivalence of the N-alkyl substituents due to partial double bond character around C-N bond in the *cis*-configuration.

Interestingly the infrared spectra (in solution and in solid state) of tris complex, SnCl $(SOCNEt_2)_3$, as well as tetrakis ones, $Sn(SOCNEt_2)_4$, display another intense band in the carbonyl stretching region in addition to the broad band due to coupled (C—O + C—N) stretching vibrations; this has been ascribed to the presence of also unidentate sulfur bonded monothiocarbamate moiety. This is further substantiated by ^{1}H NMR spectra which show two sets of widely separated complex quartets due to -CH_2 -protons of Et_2 -(N) groups in 2 : 1 and 1 : 1 intensity ratios for the tris- and the tetrakis derivatives respectively. On the basis of the available evidence octahedral configuration may be proposed to chlorotin (IV) tris- and tin (IV) tetrakis- (N, N-diethylmonothiocarbamates). With the data in hand it is not possible to comment on the relative orientation of the monodentate ligands.

Monoorganotin (IV) complexes, $RSn(SOCNEt_2)_3$, (found to be monomeric) appear to involve 7-coordinated tin as evinced by their infrared and ^{1}H NMR data. The ^{13}C NMR spectrum of n-BuSn $(SOCNEt_2)_3$ complex further substantiates the facts as it display only

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one resonance due to carbon of COS moiety and two resonances of equal intensity due to carbons of $-CH_2-$ of Et_2-(N) groups. The variation in the coordination number of tin by replacing chloro-by organo group cannot be rationalized in terms of the electronic effects.

The conducting behaviour of the halotin (IV) N, N-dialkylmonothiocarbamates in donor as well as in solvents of high dielectric constant has been examined. The trihalo-and dihalo ones exhibit substantial molar conductances in acetonitrile in the order Cl > Br > I. The formation of ionic species in solution has been proved by isolating pyridine adducts of the type $[S_nX_{4-(n+1)}(C_5H_5N)-(SOCNR_2)_n]^+X^-$ (n = 1, 2) which show the characteristic infrared bands of the coordinated pyridine molecule.

II. *Silicon (IV) Germanium (IV) Titanium (IV) and Zirconium (IV) Derivatives of N, N-Dialkylmonothiocarbamate* : The complexes of the types $MCl_2(SOCNR_2)_2$ and $ZrCl_{4-n}(SOCNR_2)_n$ [M = Si, Ge and Ti; R = Me, Et, i-Bu; n = 2 - 4] have been synthesized. The attempts to isolate $MCl_3(SOCNR_2)$ complexes were not successful. In the cases of silicon (IV) and germanium (IV) derivatives the reactions of tetrachlorides with sodium salts could not proceed beyond the formation of the bis products. All the complexes were crystalline solids. Molecular weight data of the di-iso-butylmonothiocarbamates as determined cryoscopically in benzene suggest their unimolecular nature.

The infrared spectra of the dichlorosilicon (IV) bis-(N, N-dialkylmonothiocarbamates) display no band in the region higher than $\sim$1470 cm^{-1} showing unidentate attachment of monothiocarbamates through the oxygen only. This is substantiated by the presence of ν(C = S) and ν(Si-O) vibrations in the regions 1091 ± 7 and $976 \pm 3 cm^{-1}$ respectively. A tetrahedral structure for the dichlorosilicon (IV) complexes is consistent with the observations.

The infrared spectra of all the complexes of germanium (IV), titanium (IV), and zirconium (IV) indicate the bidentate attachment of the ligand moiety. The dichloro complexes may be *cis*-octahedral geometry as evinced by two (M-Cl) stretching vibrations in their far infrared spectra. The ^1H NMR spectrum of $GeCl_2(SOCNEt_2)_2$ exhibits a quartet and a triplet indicating equivalence of Et_2-(N) groups at the probe temperature. However, the complexes of titanium and zirconium $MCl_2(SOCNEt_2)_2$, show overlapping quartets and triplets possibly due to the hindered rotation around C-N bond in the *cis*-octahedral structure. The chlorozirconium (IV) tris (N, N-dialkylmonothiocarbamates),

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$ZrCl(SOCNR_2)_3$ and zirconium (IV) tetrakis (di-iso-butylmonothiocarbamates), $Zr(SOCN\ i\text{-}Bu_2)_4$ complexes appear to be the examples of seven and eight coordinate zirconium (IV) complexes respectively.

III. *Niobium (V) and Tantalum (V) Derivatives of N, N-Dialkyl monothiocarbamate* : The reactions of pentachlorides of niobium (V) and tantalum (V) with sodium salts of monothiocarbamates did not furnish successive replacement products. The only compounds isolated was apparently bis-substituted derivatives, $MCl_3(SOCNR_2)_2$ (M = Nb, Ta; R = Me, Et, i-Bu), from the reactions of sodium salts of monothiocarbamates with metal pentachlorides in 1:2 molar ratio at room temperature in dichloromethane. The attempts to introduce more than two ligands resulted into the mixtures; the components could not be separated due to common solubility in solvents. Chromatographic separations could also not be carried out due to extremely sensitive nature of the products towards oxygen and moisture. A green sulfide of the composition, $MS(SOCNR_2)_3$ (M=Nb, Ta), however, was obtained from the reactions of metal pentachlorides with sodium salts of N, N-dialkylmonothiocarbamates in 1:4 molar ratio in refluxing benzene. All the compounds were crystalline solids, soluble in solvents other than aromatic and aliphatic hydrocarbons.

The trichloroniobium (V) and tantalum (V) bis complexes, $MCl_3(SOCNR_2)_2$, were found to behave as 1:1 electrolytes in acetonitrile and nitrobenzene; the values were found to increase with decrease in the concentration possibly due to some dissociation of ion pairs in the solutions. The molecular weights of the complexes in nitrobenzene were found to be much different than expected for the non-ionic species. On the basis of available data an ionic structure, $[M(SOCNR_2)_4]^+[MCl_6]^-$, may be proposed for these derivatives. The characteristic infrared absorptions due to hexachloroniobate and-tantalate anions were observed at 334 ± 1 and 315 ± 1 cm^{-1} respectively even in the solid state. The bidentate mode of the monothiocarbamate moiety was reflected in their infrared spectra.

The ^1H NMR spectra of the N, N-dimethylmonothiocarbamate complexes at ambient condition exhibit interesting patterns. The niobium complex shows four methyl resonances of almost equal intensity suggesting slow ligand exchange if exist in the possible C_{2v} or C_2 stereoisomers of dodecahedral geometry. The tantalum(V) analogue, however gives only two methyl resonances of equal intensity. With the limited data in hand, the spectral difference of the patterns from niobium to tantalum complexes cannot be rationalized. However, for the tanlalum

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products if it involves a dodecahedral structure facile ligand exchange in the C_{2v} or C_2 stereoisomers or the dominance of D_{2d} stereoisomers can be conjectured. In the situation, these complexes can be tentatively considered to involve stereochemical rigidity with the respect to ligand exchange at the NMR time scale.

Monomeric sulfide complexes, $MS(SOCNMe_2)_3$ (M = Nb, Ta), may have 7-coordinated central metal atoms. A strong band in their far infrared spectra at 503 and 481 cm^{-1} may be assigned respectively to (Nb = S) and (Ta = S) stretching vibrations in addition to ν (M—S-) (M = Nb, Ta) vibrations observed in the region 361-365 cm^{-1}.

IV. *Tin(IV) Derivatives of Monothiocarbonate* : The reactions of potassium salts of monothiocarbonates with tin(IV) halides and organotin(IV) chlorides have furnished products of the types, $SnX_2(SOCOR)_2$, $R_2'SnCl_{2-n}(SOCOR'')_n$, $R_3'Sn(SOCOR'')$ (X = Cl, Br, I; R = Et, — p-tolyl; R′ = Me, n-Pr, n-Bu; R″ = —p-tolyl; n = 1, 2). The organotin(IV) complexes of ethylmonothiocarbonate were found to be thermally unstable. All these complexes were crystalline solids or liquids, soluble in common organic solvents excepting dihalotin (IV) bis(ethylmonothiocarbonates) which were soluble only in acetonitrile. The molecular weights determined cryoscopically in benzene suggest unimolecular nature of the complexes.

In distinction to dihalotin(IV) bis(aromaticmonothiocarbonates), the analogous bis(ethylmonothiocarbonates) show some molar conductance in acetonitrile in the order Cl > Br > I. This behaviour may be associated with the solvolysis as shown by the isolation of a pyridine compound of the type $[SnBr(C_5H_5N)—(SOCOEt)_2]^+ Br^-$. The deviation in the behaviour of the dihalotin(IV) bis(ethylmonothiocarbonates) complexes in the solution from that of aromaticmonothiocarbonate analogues may be attributed to the weak complexation behaviour of ethylmonothiocarbonate moiety.

In contrast to all other tin(IV) derivatives, the triorganotin(IV) complexes in their infrared spectra display a sharp and strong absorption at higher frequency around 1608±3 cm^{-1} owing to ν (C=O) vibrations indicating somewhat anisobidentate mode of bonding of monothiocarbonate moiety with weak Sn—O interaction. The presence of two absorptions assignable to asymmetric and symmetric (Sn—C) stretching vibrations show nonplanarity of the organo groups bonded to central tin atom. The ^1H NMR spectra of trimethyltin(IV) (p-tolylmonothiocarbonate) show $^{119}Sn—^1H_{CH_3}$ coupling constant (J) of the order of ~ 60 Hz suggesting a coordination number for the tin in between 4 and 5.

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In the infrared spectra of dihalo- and diorganotin(IV) complexes the ν (C—O) modes can be seen in the region 1595±5 cm^{-1} due to the chelating nature of the monothiocarbonate ligands. In the bis complexes, the presence of two absorptions in the far infrared region [ν_{as}(Sn-Cl) at 328±3 and ν_s(Sn-Cl) 311±4 cm^{-1}; ν_{as}(Sn-C) at 383±8 and ν_s(Sn-C) at 519±9 cm^{-1}] may arise due to non-linearity of Y-Sn-Y (Y = Cl or C) moiety. The ^1H NMR spectrum of dimethyltin(IV) bis(p-tolylmonothiocarbonates) show ^{119}Sn-$^1H_{CH_3}$ coupling constant (J) value to be 79 Hz corresponding to 6-coordinate tin.

The X-ray powder diffraction pattern for diphenyltin (IV)—bis (p-tolylmonothiocarbonates) has been examined. The observed diffraction lines could be indexed for orthorhombic symmetry. The lattice parameters computed for the above symmetry were a = 16.80A, b = 13.40 °A, c = 12.49 °A; V = 2814 $^{\circ}\text{A}^3$, Z = 4. Efforts are in progress to carry out single crystal X-ray analysis for full structure of the compound.

Ab Inito MO CALCULATIONS OF NUCLEAR QUADRUPOLE COUPLINGS

Vijaya Keshari Sup. *Dr. P. Chandra*

This thesis deals with the evaluation of nuclear quadrupole coupling constants, using *ab initio* mo method. The quadrupole coupling arises due to the interaction of the electrical field gradient (surrounding electrons and nuclei) with nuclear quadrupole moment. This can be observed experimentally by

(i) molecular beam microwave spectroscopy,

(ii) pure quadrupole spectra of solids, and

(iii) in case of gases by rotational spectra.

Nuclear quadrupole coupling constant is the product of eq (electric field gradient) and Q (quadrupole moment) of coupling nucle and is represented as eqQ or eq_{zz}, where z—axis is taken as the principal axis of the system. Q(quadrupole moment) is taken as constant from literature and has dimension of area, and is of the order of 10^{-24} cm^2. The quantity q_{zz} (is the second derivative of the potential), field gradient, is of the order of 10^{17} V/cm^2, which is a very high field to produce in the laboratory. Such a high field can be observed in solids as crystal field, e is the proton charge.

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In our study, we have used *ab initio* mo method to calculate the quadrupole couplings in D_2, DF, DCl, CO, N_2, ClF, DCN, DNC, D_2O, D_2CO and CD_4 molecules. This thesis which is divided in four chapters, embodies the result of these calculations. In the first chapter, a general introduction, a brief historial survey of the quadrupole coupling and general theory of electric field gradients and quadrupole coupling constants are discussed.

Second Chapter of this thesis describes the use of linear combination of the Gaussian orbitals (LCGO) method in SCF calculations. General expressions for overlap, kinetic energy, nuclear attraction, field gradients and electron repulsion integrals are listed in this chapter and a brief description of the computer program written for the evaluation of quadrupole couplings is given.

In our calculations, we have used the (9s5p)/[3s2p] and 4s2p basis sets for first row atoms and (4s)/[2s] on hydrogen except for chlorine, where (11s7p)/[6s4p] basis sets were used. For few cases, different basis sets have been used to test the suitability of the basis sets.

Chapters III and IV deal with the calculations of total energy and and quadrupole coupling constants. In Chapter III, the effect of basis sets on the energies and quadrupole coupling constants are given for D_2, DF, DNC and D_2O molecule. Our calculations reveal that for such calculations the use of bond centered functions along with double-zeta (9s5p)/[4s2p] basis functions with contraction [4321; 32] on first row atom and (4s)/[2s] on hydrogen with $H=2.0$ give better results compared to the larger basis sets such as (10s6p)/[5s4p] on first row atom and (5s)/[3s] on hydrogen with scale factor 2.0.

In Chapter IV, we have discussed the calculations of quadrupole coupling constants and total SCF energy for CO, N_2, DCl, ClF, DCN, D_2CO and CD_4 molecules with(9s5p)/[3s2p] or [4s2p] basis sets for first row atoms and (11s7p)/[6s4p] for chlorine. The total energy values are very nicely reproduced compared to other *ab initio* calculations and experimental results (wherever available). Calculated quadrupole coupling constants are encouraging for heavier nuclei such as ^{14}N, ^{17}O and ^{35}Cl, but for deuteron quadrupole couplings the results are not very satisfactory.

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STUDIES ON SOME ASPECTS OF PREPARATION AND SOLUBILITY EQUILIBRIA OF SOLID SOLUTIONS OF HYDROXYL AND CHLORAPATITE OF ARSENIC

Preeti Lahiri Sup : *Dr. T. S. B. Narsaraju*

Calcium hydroxylapatite (CaHA), $Ca_{10}(PO)_4)_6(OH)_2$, the principal inorganic constituent of human bones and teeth, belongs to an isomorphous series of substances known as "Apatites." It has been the subject of extensive investigations by virtue of its biological significance and its remarkable ability to undergo a series of cationic and anionic exchange reactions. Significant among its anionic exchange reaction is the complete replacement of PO_4^{3-} by AsO_4^{3-} leading to the formation of arsenic hydrozylapatite, an isomorph of hydroxylapatite.

Inhalation of arsenic in the form of dust or fumes leads to an occupational disease known as "Arsenic poisoning." Since Cl^- ion is available in the human body fluids as well as in dental enamel, bones and teeth, there is a possibility of exchange of OH^- ion by Cl^- ion (ionic radii 1.68 and 1.82 A^0 respectively) resulting thereby in the formation of arsenic chlorapatite (AsClA), an isomorph of AsHA. Partial isomorphous replacement of the OH^- ion by Cl^- ion in the body fluids results in the formation of a series of solid solutions of AsHA and AsClA. The principal bone processes, calcification and resorption, are concerned respectively with the deposition and dissolution of OHAp at the bone body-fluid interface. Solubility studies of AsHA, AsClA and their solid solutions under simulated biological conditions is therefore considered desirable to explore a possibility of a reversal of such an incorporation.

Using calcium nitrate and diammonium hydrogen arsenate as starting materials, a sample of AsHA was prepared by a wet method in a highly alkaline medium. Based on a solid states reaction samples of AsClA and its solid solution with AsHA were prepared at 1060°C using calcium chloride and AsHA as starting materials. The homogeneity and purity of the samples were confirmed through x-ray, electronmicroscopic and i. r. studies supplemented by chemical analyses. A systematic dilation of the unit cell with an increase in the Cl^- eontent in the solid solution was observed. A linear dependence of unit cell volume on the proportion of AsClA was observed substantiating the validity of Vegard's law, a criterion for the formation of solid solutions. The electronmicrographs of the samples

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revealed the characteristic hexagonal patterns of the crystals confirming thereby the absence of extraneous phases. IR absorption spectra recorded in the range, 4000-650 cm^{-1} show the presence of AsO_4^{3-} and OH^- peaks at 845 cm^{-1} and 3600 cm^{-1} respectively. A shift in the wave number of the peak in the range, 3525 to 3575, was found for the solid solutions. It can be attributed to a perturbation of the stretching mode of vibration of OH^- ions caused by the yrssence of Cl^- ions in their proximity. Such a perturbation effect was found to disappear in the case of AsClA, confirming thereby complete replacement of OH^- by Cl^-. It has been found through chemical analyses of apatites that the samples bear a atom ratio Ca/As, close to stoichiometry.

The solubility equilibria of hydroxyl and chlorapatite of arsenic and a series of their solutions were investigated at 37°C as a function of pH in the range, 4.7 to 7.4. From systems consisting of equilibrated powdered samples of the solutes with appropriate buffer solutions, the colloidal component was separated through filtration using 1G4 sintered glass crucibles. The filtrates were subjected to microanalytical determinations of the concentration of the dissolved ions. The minimum duration of equilibration required for the attainment of saturation was established through studies on the dissolution kinetics. Based on the consideration that orthoarsenic acid exhibits three stages of dissolution the total amount of arsenic determined was subdivided into proportions of the undissociated acid as well as of the products of dissolution $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}, the three dissociation constants of the acid as well as the final pH being employed for the purpose. Out of these values, the concentration of AsO_4^{3-} ion was desired for the calculation of the ionic product of the solute While Ca^{2+} ion concentration was determined complexometrically, the OH^- ion was evaluated from the measured pH values. By maintaining concentration of sodium nitrate equal 0.165 M in the medium of dissolution it could be ensured that the ionic strength remained virtually constant throughout dissolution of the solute enabling its ionic product, K_{ip}, to be considered as its solubility product, K_{sp}.

Based on the molecular formulae of the solutes, the corresponding ionic products were calculated making use of the sets of concentration of the products of dissolution at different pH values. At a constant temperature, the ionic product of each solute was found to be constant in spite of the fact that pH of the medium of dissolution was varied. Proof for the occurrence of stoichiometric dissolution of the samples could be obtained on the basis of (i) the constancy in the pK_{ip} values of the apatite phase, (ii) the agreement of the g atom ratios, Ca/As

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total, of the saturated solutions with the theoretical value, (iii) the precise response of the Ca/As total values to the addition of common ions and (iv) the inability of the slurry density, the solute to solvent ratio, to function as a parameter in influencing the extent of solubility.

A comparative study of the solubilities of the samples could show that AsClA was less soluble than AsHA and that the solid solutions exhibited an intermediary behaviour showing a systematic decrease in the solubility with an increase in their chloride content. An explanation of these results could be provided on the basis of hydration and lattice energies of ionic solids consequent upon isomorphous anionic substitution.

SYNTHESIS AND STRUCTURAL STUDIES ON TERNARY COMPLEXES OF THE BIVALENT 3d METAL IONS WITH UNINEGATIVE BIDENTATE LIGANDS

Ram Lakhan Prasad Sup. : *Dr. R. C. Agrawal*

In recent years there has been an upsurge of interest in the study of the ternary complexes whery two or more different ligands are disposed in regular or pseudo-regular geometry around central metal ion in any of its possible oxidation state. There is considerable change in the properties of coordinated ligands in the ternary complexes as compared to the binary chelates of these ligands.

A careful literature survey in the first introductory chapter reveals that most of the work that has been carried out on the ternary complexes of uninegative bidentate ligands is confined to determination of their stability constants in solution. There are only few publications dealing with the synthetic and structural aspects of these complexes. Due to inadequacy or complete absence of previous work on the ternary complexes of oxovanadium(IV), manganese(II), cobalt(II), nickel(II), copper (II) and zinc(II) with uninegative bidentate ligands like acetylacetone (acacH), benzoylacetone (bacH), dibenzoylmethane (dbmH), 2-aminobenzoic acid (abH), salicylaldoxime (saloxH), 1-nitrose-2-naphthol (NNphH), dithiocarbamate (dtc^-), xanthate (xan^-), dimethylglyoxime (dmgH), salicylaldehyde phenylhydrazone (sphH), synthetic and structural studies of these complexes were undertaken and results of these studies are described in chapters III to VI.

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Preparation and Analysis of the Complexes

The ternary complexes have been prepared either by the replacement of one of the coordinated ligands in the binary complex by another ligand or by an *in situ* reaction of metal(II) salt, the two ligands and sodium hydroxide in 1 : 1 : 1 : 2 molar ratio in appropriate solvent. Pyridine adducts have been obtained by the addition of excess pyridine to an ethanolic solution of the ternary complexes.

The ternary complexes and their pyridine adducts have been analysed for metal, sulphur, carbon, hydrogen and nitrogen. Structure of the ternary complexes and their pyridine adducts have been investigated by conductance, magnetic susceptibility, infrared, electronic, proton magnetics resonance and electron spin resonance spectral studies. The analytical data show the formation of the ternary complexes of the general composition MLL'.nH_2O (n=0, 1, 2) and bis pyridine adducts.

Magnetic Moments

Room temperature magnetic moments of most of the cobalt(II) complexes are in the range reported for spin-free octahedral stereochemistry. The μ_{eff} values of Co(NNph) (ab), Co(acac) (NNph) .H_2O, Co(acac) (NNph) and Co(NNph) (salox) are subnormal. The complexes Ni(dtc) (xan), Ni(dtc) (salox), Ni(dtc) (dmg), Ni(xan) (dmg), Ni(xan) (salox) and Ni(dmg) (salox) are diamagnetic showing thereby their square planar stereochemistry. The μ_{eff} values of most of the paramagnetic nickel(II) complexes lie well within the range expected for octahedral geometry. However, in some cases like Ni(acac) (NNph) .H_2O Ni(acac) (NNph), Ni(acac) (salox), Ni(NNph) (salox) magnetic moments are much lower than those reported for octahedral nickel(II) complexes.

Electronic Spectra

Electronic spectra of oxovanadium(IV) complexes generally show two bands in the regions 11000 and 15500-20000 cm^{-1} assigned to d_{xz}, $dyz \leftarrow d_{xy}$ (ν_1) and $d_x2_{-}y2 \leftarrow d_{xy}$ (ν_2) transitions respectively on the basis of distorted octahedral geometry.

Electronic spectra of cobalt (II) complexes usually exhibit two d-d transitions in the regions 8000-11000 and 18000-20000 cm^{-1} assigned to $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ (ν_1) and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ (ν_3) respectively, assuming octahedral geometry. Since, $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$ (ν_2) transition is an essentially two electron process, it is weaker by about a factor 10^{-2} than the other two transitions (ν_1 and ν_3). This weakness combined with its

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close proximity to ν_3 results in the non-observation of this band. The ν_3 band is observed as a shoulder only in the complexes Co(acac) (salox) and Co(acac) (salox).2py in the range 15000-15500 cm^{-1}.

Three d-d transition bands have usually been observed in the case of nickel(II) ternary complexes in the ranges 9000-10500, 15000-16000 and 22000-26000 cm^{-1} assigned to $^3T_2g(F) \leftarrow {}^3A_2g(F)$ (ν_1), $^3T_1g(F) \leftarrow {}^3A_2g(F)$ (ν_2) and $^3T_1g(P) \leftarrow {}^3A_2g(F)$ (ν_3) transitions respectively. These spectral features are consistent with octahedral geometry around nickel (II). The diamagnetic nickel(II) complexes of dtc^- or xan^- show three bands in the regions 15000-16000, 18000-20000 and 23000-25000 cm^{-1} assigned to $d_{x^2-y^2} \leftarrow d_{xy}(\nu_1)$, $d_{x^2-y^2} \leftarrow d_{xz}$, $d_{yz}(\nu_2)$ and $d_{x^2-y^2} \leftarrow d_{z^2}$ (ν_3) transitions on the basis of square planar geometry. However, in the case of Ni(dmg) (salox) only ν_1 and ν_2 are observed at 18520 and 24600 cm^{-1} respectively. In general, ν_2 band is broad, but in some cases as in Ni(xan) (dmg), this band splits into two components due to the splitting of e_g level caused by asymmetry of the ligand field. Electronic spectrum of Ni(acac) (salox) exhibits d-d transition bands at 11110, 15153 and 23530 cm^{-1} and a shoulder at 16400 cm^{-1} indicating octahedral-square planar or spin free-spin paired equilibrium.

Electronic spectra of copper(II) complexes show d-d transition bands in the ranges 14000-16000, 18000-20000 cm^{-1} and 23000-28000 cm^{-1} assigned to $d_{x^2-y^2} \leftarrow d_{xy}$ (ν_1), $d_{x^2-y^2} \leftarrow d_{z^2}$ (ν_2) and $d_{x^2-y^2} \leftarrow d_{xz}$, d_{yz} (ν_3) transitions respectively on the basis of distorted octahedral geometry. In some cases ν_3 band mixes with charge-transfer ligand band and is not observed. Extent of distortion from octahedral geometry as evaluated from ν_{Cu}/ν_{Ni} ratio comes out to be >1.45 indicating extremely high distortion approaching square planare geometry of the complexes.

A close similarity in the positions and shapes of bands in the spectra of dipyridine adducts, aquo and anhydrous complexes indicates that there is no change in geometry around metal ions.

ESR Spectra

The room temperature as well as frozen chloroform solution ESR spectra of copper(II) and oxovanadium(IV) complexes have been studied. The LNT spectra show clearly resolved parallel and perpendicular features.

The g_{iso} values of copper(II) complexes are in the range reported for square planar complexes. In the case of Cu(acac) (ab), Cu(acac) (salox), Cu(NNph) (salox), Cu(acac) (bac) and Cu(bac) (dbm) the g

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values follow the trend $g\mu > g\perp > g_e$ (free electron value), suggesting that the unpaired electron lies in $d_{x^2-y^2}$ orbital of copper(II). However, in the case of Cu(acae) (dbm) the g values show the trend $g\perp > g_u > g_e$ (free electron value), indicating that the unpaired electron lies in d_{z^2} orbital of metal ion. Calculation of molecular orbital coefficients α^2 and β^2_1 shows greater covalency in the ternary complexes as compared to their simple binary complexes.

The g values in vanadyl complexes lying in the order $g\mu < g\perp < g_e$ (free electron), suggest that the unpaired electron is present in d_{xy} (b_{2g}) orbital of vanadium. The isotropic hyperfine coupling constants suggest lees localisation of electron on the metal orbital of the ternary complexes as compared to bis binary complexes.

The difference in A_{iso} between any two copper(II) complexes is found to be higher than that between the two corresponding oxovanadium(IV) complexes. This indicates that metal to ligand charge transfer is more favoured in the former complexexs than the latter.

PMR Spectra

PMR spectra of Zn(acac) (bac) and Zn(acac) (dbm) are consistent with expected stoichiometry of the ternary complexes. The extent of redistribution of electron density between the two ligands in the ternary complexes has been inferred from a comparison of the positions of methine protons in the binary and ternary complexes and from these studies the relative μ-acceptor ability of β-diketonates has been found to be :

$$dbm^- > bac^- > acac^-$$

From the position of ortho-phenyl protons, it has been concluded that phenyl ring is oriented in the plane of coordinated β-diketonate ring.

IR Spectra

The bonding sites of the ligands involved in the ternary eomplexes have been inferred ftom a careful comparison of IR spectra of the ternary complexes in nujol and KBr with the spectra of the binary complexes and the parent ligands.

The ν (C—O) and ν (C—C) modes of vibration of $acac^-$, bac^- and dbm^- are observed in the ternary complexes involving one of them or any two of them as ligands in 1575-1610 and 1500-1530 cm^{-1} regions respectively. The presence of only one band for the above modes shows that the bond order of the two C—O bonds as also the two C—C bonds

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in the ternary complexes are identical indicating thereby uninegative bidentate nature of these ligands.

Infrared spectra of sodium 2-aminobenzoate exhibits four absorptions at 3436, 3330, 1521 and 1398 cm^{-1} assigned to ν_{as}(N-H), ν_s(N-H), $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ modes respectively. Negative shifts in ν_{as}(N-H) (56-116 cm^{-1}), ν_s(N-H) 180-210 cm^{-1}), $\nu_s(COO^-)$ (8-18 cm^{-1}) and positive shift of (9-27 cm^{-1}) in $\nu_{as}(COO^-)$ in the spectra of hydrated ternary complexes, pyridine adducts involving 2-aminobenzoate (ab^-) as one of the ligands, as compared to sodium salt of this ligand indicate that nitrogen of the amino group and oxygen of the carboxylate group are involved in bonding and ab^- functions as a uninegative bidentate ligand. Further, positive shift in $\nu_{as}(COO^-)$ (9-14 cm^{-1}) as well as $\nu_s(COO^-)$ ($\sim$7 cm^{-1}) together with negative shifts in ν_{as}(N-H) (50-100 cm^{-1}) and ν_s(N-H) (150-200 cm^{-1}) in anhydrous ternary complexes containing ab^- as one of the ligands indicate bridging tridentate behaviour of ab^-

The following additional inferences have been drawn from IR spectra :

The decrease in $\nu(V=O)$ frequency in the ternary complexes of oxovanadium (IV) suggests following relative order of donor strength of the ligands :

$$NNph^- > salox^- > ab^- > acac^-$$

The magnitude of shifts in ν(C—O) of the $acac^-$ in M(acac)(ab) and M(acac) (salox) complexes suggests that $salox^-$ is a better π-acceptor than ab^-.

SYNTHETIC STUDIES ON SOME SULPHUR COMPOUNDS

Ramesh Chandra Sup. *Dr. P. K. Srivastava*

The importance of sulphur compounds as potent medicinal agents is well known. Although much work has been already done on potentially biologically active sulphur compounds, but there is still enough scope for further probe.

Various symmetrical and asymmetrical triazines and their derivaatives have been prepared earlier and fruitfully tested against their antibacterial, antifungal and anticancer properties. So 1,4-diaryl-1,6-dihydro-1,3,5-triazine-6-thione, the less explored system, has been taken

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up as the main nucleus or base moiety in the synthesis of some thiocarbamides, thiosemicarbazides, mercaptans and Schiff bases as possible antithyroid, antifungal & antibacterial agents respectively.

The thesis is broadly divided into the following four chapters including "General introduction."

The first chapter is an account of various classes of important sulphur compounds having potential biological activity. This is essentially in the form of a brief review highlighting structural considerations in relation to biological activity.

The second chapter deals with the preparation of various 1-aryl-2-alkyl-mercapte-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thiones by the interaction of benzoyl isothiocyanate with s-alkyl-N-aryl-isothiocarbamides.

The degradative studies on s-triazine thione has been also carried out to furnish a direct evidence in favour of its structure, derived earlier indirectly by Goerdeler and Neuffer.

2-Amino/anilino- derivatives of s-triazine thione were obtained by refluxing it with ammonia/amines in equimolar quantities. 2-Amino-1-aryl-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thione thus formed on treatment with different isothiocyanates afforded related thioureas.

Similarly 1,4-diphenyl-1,6-dihydro-1,3,5-triazine-6-thione on treatment with hydrazine hydrate at room temperature afforded corresponding 2-hydrazino derivative which in turn gave related thiosemicarbazides On interaction with different isothiocyanates.

Few of N-aryl/alkyl-N'-(1-aryl-4-phenyl-6-thioxo-1,6-dihydro-1,3,5-triazin-2-yl) thioureas thus synthesised were also tested against their antithyroid activity.

Third chapter describes the synthesis of 1-aryl-4-phenyl-2-mercapto-1,6-dihydro--1,3,5-triazine-6-thione by the deal-kylation of 1-aryl-2-benzylmercapto-4-phenyl-1,6-dihydro-1,3,5-triazine-6-thione by means of thiourea and hydrochloric acid.

These mercaptotriazines were latentiated with α,β-unsaturated carbonyl compounds, cyanamides and diaryl carbodiimides. This was done on the assumption that latentiation might improve the antithyroid and antiradiation property of already known drugs and that the adducts thus formed might hopefully revert back to the original thiols at a biologically appropriate site in the body.

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Latentiation of z-mercaptotriazines was achieved by refluxing it with different α,β-unsaturated carbonyl compounds in equimolar ratio in ethyl acetate.

Interaction of arylcyanamides with mercaptotriazines provided us an attractive route for the synthesis of N-aryl-s-(1-aryl-4-phenyl-6-thioxo-1,6-dihydro-1,3,5-triazin-2-yl)-isothiouronium hydrochlorides.

We were also able to extend this addition reaction of mercaptotriazines with diarylcarbodiimides. Isothiouronium salts, the adducts were obtained by mixing cold solution of mercaptotriazine in acetone with a cold solution of carbodiimides in acetone and passing dry HCl gas in the reaction mixture.

Chapter Four deals with the synthesis and biological screening of some Schiff bases containing triazinyl moiety. Compounds were synthesised by adopting two different schemes.

First scheme leads to the formation of s-(1-aryl-4-phenyl-6-thioxo-1,6-dihydro-1,3,5-triazin-2-yl) thioacetyl-N-benzylidene hydrazines.

Following carbonyl compounds were used in the condensation;

o-Salicylaldehyde, *p*-chlorobenzaldehyde, *m*-nitrobenzaldehyde, NN'-dimethyl-*p*-aminobenzaldehyde, acetophenone, isatin.

By adopting another sequence of reactions few N-(1-aryl-4 phenyl-6-thioxo-1,6-dihdro-1,3,5-triazin-2-yl)-N'-benzylidene hydrazines were also synthesised.

Few compounds of this class were screened against their antibacterial and antifungal properties.

COMPLEXATION BEHAVIOUR OF DIORGANOTIN (IV) CATIONS AND A FEW OTHER TETRAVALENT ELEMENTS WITH SOME BIDENATE LIGANDS

Geeta Singh Sub. : *Dr. V. D. Gupta*

Organometallic compounds have reached the stage of extensive applications in industry, agriculture and laboratories. Toxic and biological properties of some are significant and interestingly distinct from those of the metals from which these can be derived. Some of the organometallic compounds may be involved in environmental mobiliza-

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tion and transport of metals. In this context the understanding of the existence and complexation of organometallic cations in solution is critical and significant. There are four organometallic ions derived from Hg, Sn, Pb, and Tl which are found to exist in aqueous medium. Biomethylation of mercury and complexation of organomercury have been extensively examined. Apart from mercury very little information is available for the other organometallic species. Organothallium cations are evidently too unstable for definite characterization. In organolead species the Pb-C bond is not much stronger. Behaviour of diorganotin (IV) cations has been examined in aqueous solution.

In the course of the present investigation complexation of diorganotin (IV) ions with N-arylbenzhydroxamic acids, β-diketones and their thio analogues have been studied potentiometrically. Subsequently, thermodynamic parameter have been computed to shed more light on the complexation behaviour of the ligands towards diorganotin (IV) cations. In addition to this work a few organotin (IV), organosilicon (IV), germanium (IV), and cyclopentadienyltitanium (IV) complexes of N-arylbenzhydroxamic acids have been prepared by different routes in nonaqueous solvents. On the basis of molecular weight and IR and PMR spectral measurements, plausible structures have been proposed. The X-ray powder diffraction pattern of a dimethyltin (IV) complex PhCON-p-toly10)$_2$ $SnMe_2$ has been examined. The work described in the thesis can be summarized under the following heads :

1. Potentiometric determination of dissociation constants, successive stepwise formation constants and thermodynamic parameters of diorganotin (IV) complexes—
   A. With N-arylbenzhydroxamic acids.
   B. With β-diketones.
   C. With monothio- β -diketone.
2. Synthesis and characterization of diorganotin (IV) and cyclopentadienyltitanium (IV) derivatives of N-arylbenzhydroxamic acids.
3. Synthesis and characterization of organosilicon (IV) and germanium (IV) derivatives of N-arylbenzhydroxamic acids.

1. **Potentiometric Determination of Dissociation Constants, Successive Stepwise Formation Constants and Thermodynamic Parameters of Diorganotin (IV) Complexes.**

A. *With N-Arylbenzhydroxamic Acids* : The complexation behaviour of diorganotin (IV) ions with N-arylbenzhydroxamic acids

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have been studied potentiometrically in 75%(V/V) dioxan-water medium at different temperatures (20°, 30° and 40°C) and at constant ionic strength, 0.1 M (NaCl), in nitrogen atmosphere. The specific medium was chosen to avoid even the minimum possibility of hydrolysis of diorganotin (IV) dichlorides. A mixture of solution containing N-arylbenzhydroxamic acid (0.01 M), dialkyltin dichloride (0.0025 M) and sodium chloride (0.01 M) was titrated against sodium hydroxide (0.1 M). Correction factor (log $U_H = 0.08$, 0.13 and 0.17 at 20°, 30° and 40° ± 0.1°C) was added to the observed pH. The stoichiometric and thermodynamic formation constants (pq_D and pK_D) of the above metal-ligand system have been determined by interpolation at half $\bar{n}$ values and Correction-term and Leasts-quare methods. Since the formation constant data obtained from all three methods were in good agreement, the data computed from Least square method were used to calculate the thermodynamic parameters such as $\triangle G^\circ$, $\triangle H^\circ$, $\triangle S^\circ$ and $\triangle Cp^\circ$ of the complexation reactions.

The first formation constant of dialkyltin (IV)-N-arylbenzhydroxamate systems at particular temperature has been found to increase with the change of alkyl group from methyl to butyl in R_2Sn (IV) moiety probably due to the increase in the electrophilic character of tin atom with increase of the chain of alkyl groups bonded to it. It has also been observed that the formation constants display increasing trend with the rise in the temperature of the system suggesting that complexation reaction is more favourable with increase in temperature in these systems. A comparatively higher values of formation constant of diorganotin (IV)-N-p-tolylbenzhydroxamate system in comparison to N-phenylbenzhydroxamate system suggest that complexation of N-p-tolylbenzhydroxamic acid is more favoured.

The increasing trend of negative $\triangle G^\circ$ values with rise in temperature coupled with positive $\triangle H^\circ$ values substantiate the finding that complexation reaction in diorganotin (IV)-N-arylbenzhydraxamate system is favourable at higher tempertature. A comparatively higher positive values of $\triangle S^\circ$ in comparison to $\triangle H^\circ$ indicated that entropy is the driving force for the formation of the metal complexes. The plot of the values of log β *vs* T^{-1} has been found to be a straight line indicating zero value of $\triangle Cp^\circ$

A few complexes have been separated from 75% (V/V) dioxan-water medium to substantiate the nature of diorganotin (IV) species formed in the system. The bis products Me_2SnL_2 isolated are sharp melting crystalline solids and exist as monomer (cryoscopically in

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benzene). The PMR spectra in $CDCl_3$ show J^{119} Sn-CH_3 value to be 80 Hz (L = PhCON-PhO$^-$) and 78 Hz (L = PhCON-p-tolyl O$^-$) corresponding to six coordinate tin. The IR data of the products shows them to be octahedral with both ligands behaving as bidentate and organo groups occupying perhaps the trans-position.

The X-ray powder diffraction pattern for (PhCONp-tolylO)$_2$ $SnMe_2$ has been examined. The prominent diffraction lines observed could be satisfactorily indexed for tetragonal symmetry. The lattice parameters computed for the above symmetry are a = 17.48A°, c = 10.96A°. Efforts are in progress to carryout single crystal X-ray analysis of this complex for full structure in collaboration with the spectroscopic division of the Physics Department of this University.

The behaviour of thiohydroxamic acid could not be examined due to its inherent instability in solution. The studies on the complexation behaviour of β-diketones and monothio-β-diketone described succeedingly could be pursued to understand the relative affinity of oxygen and sulphur towards R_2Sn (IV) as substrate.

B. *With β-Diketones* : Dissociation constants of β-diketones (benzoylacetone and dibenzoylmethane) and successive stepwise formation constants of their complexes formed with dialkyltin (IV) ions have been determined. Like N-arylbenzhydroxamic acids, an observed increase in the value of the first formation constant data of dialkyltin (IV)-β-diketonate systems with increase in the length of the alkyl chain bonded to tin atom is accountable in terms of the increased electrophilicity of the tin atom. In contrast the increase in the value of overall formation constant with decrease in temperature suggested that the low temperature is favourable for complex formation in these systems. It may also be mentioned dibenzoylmethane appears to be a better chelating ligand in comparison to benzoylacetone for complexation with dialkyltin (IV) ions of evidenced from the observed higher value of overall formation constant. In order to substantiate our findings thermodynamic parameters such as $\triangle G^\circ$, $\triangle H^\circ$, $\triangle S^\circ$ and $\triangle Cp^\circ$ have been calculated.

To shed more light on the nature of complexes formed in the solution, crystalline bis-products, $(RCOCHCOR')_2SnR_2''$ have been isolated and characterized. The infra-red data revealed bidentate attachment of β-diketonate moiety to the central tin atom in all these complexes.

C. *With Monothio-β-Diketone* : Potentiometric study of the complexation behaviour of dialkylitin (IV) ions with a monothio-β-

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diketone has also been undertaken with a view to understand the effect of replacement of oxygen by sulphur atom on the behaviour of ligand. The dissociation constant of monothiodibenzoylmethane and successive stepwise formation constant of their complexes with dialkyltin (IV) moiety have been determined in 75% (V/V) dioxan-water at 20°, 25° and 30° ± 0.1°C. Reproducible data above 30°C could not be obtained due to decomposition of the thio-β-diketone. First formation constants of dialkyltin (IV)-monothiodibenzoylmethane system show trends similar to as noted for the dibenzyolmethane system. A comparatively higher values of first formation constant of thio system appeared to be in agreement with the greater complexation tendency of monothio-β-diketones suggesting class (b) nature of diorganotin (IV) cations. The overall formation constant of the investigated system has been found to decrease with increase in temperature showing that the complexation reaction occurs with much ease at the low temperature. The thermodynamic parameters have been computed and these support the above findings.

Yellow crystalline bis products, $(PhCSCHCOPh)_2SnR_2$, (R = Me, n—Pr, n—Bu) have been isolated from the 75% (V/V) dioxan-water medium and characterized. The bidentate mode of the bonding of monothiodibenzoylmethane moiety towards the central tin atom in these complexes has been evinced from their IR spectra.

2. Synthesis and Characterization of Diorganotin (IV) and Cyclopentadienyltitanium (IV) Derivatives of N-Arylbenzhydroxamic Acids

A convenient method for the isolation of bis N-arylbenzhydroxamate, $(PhCONRO)_2SnR_2$ (II) involves the reactions of dialkyltin (IV) oxide with the N-arylbenzhydroxamic acids. The reaction can be carried out in benzene while water is fractionated out simultaneously. IR and PMR data of the products establish the identity of these with the compounds isolated from the dioxan-water medium. Dialkyltin (IV) bis (N-arylbenzhydroxamates) undergo ligand exchange reaction with the corresponding dialkyltin dichloride in benzene at room temperature to give dialkyltin (IV) chloro (N-arylbenzhydrozamate), $(PhCONRO)SnClR'_2$, (III) which are also found to be monomeric in benzene.

$$2PhC(O)NROH + R'_2SnO \rightarrow (PhCONRO)_2SnR'_2 + H_2O$$

(II)

$$(PhCONRO)_2SnR'_2 + R'_2SnCl_2 \rightarrow 2(PhCONRO)SnClR_2$$

(III)

(R = Ph or p - tolyl ; R′ = n-Pr or n-Bu)

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Absence of νOH and substantial lowering of νC=O frequency indicate the bidentate behaviour of the ligand moiety. A trigonal bipyramidal geometry (IV) can be tentatively) suggested for them. Two R groups may be occupying the axial positions as the IR spectra seems to give only one band assignable to νSn-C absorption. PMR spectra of these complexs show multiplet due to alkyl protons in addition to the peaks observed for phenyl protons of the ligands. In the derivatives of N-p-tolylbenzhydroxamic acids a singlet is also observed due to the methyl group in the ligand.

The dicyclopentadienyltitanium (IV) derivatives of N-arylbenzhydroxamates (V) have been prepared by the reaction of dicyclopentadienyltitanium dichloride with N-arylbenzhydroxamic acid in the 1:1 and 1:2 molar ratio in the presence of triethylamine in acetonitrile.

All these are monomeric crystalline products having sharp melting points and are soluble in common organic solvents. The IR spectra show bidentate behaviour of N-arylbenzhydroxamate. All the important infra-red bands due to cyclopentadienyl moiety bonded to titanium atom have been observed. The PMR spectra showed peaks corresponding to cyclopentadienyl moiety in addition to the peaks due to the protons in the ligands. Dicyclopentadienyltitanium (IV) bis (N-arylbenzhydroxamates) suffer decomposition after few days as shown by the change in colour of the compounds from red to dark brown. Infra-red spectra of this brown product indicated the loss of cyclopentadienyl moiety.

3. Synthesis and Characterization of Organosilicon (IV) and Germanium (IV) Derivatives of N-Arylbenzhydroxamic Acids

Hexamethyldisilazane has been found to be the most successful silylating agent for N-arylbenzhydroxamic acids leading to the synthesis of mono (trimethylsilyl) N-arylbenzhydroxamate PhC(O)N-p-tolylOSiMe$_3$.

The reaction of diorganodichlorosilane with sodium salts of N-arylbenzhydroxamic acid provides easy synthetic route for diorganosilyl bis (N-arylbenzhydroxamates), [PhC(O)NRO]$_2$ SiR$_2$.

The attempt to synthesize monochlorodiorganosilyl derivative resulted in the formation of the bis product only. All the products are crystalline with sharp melting points and are monomeric. Absence of νOH shifting of νC=O at higher frequency in the infra-red spectra of these derivatives characterize them to be of tetrahedral geometry with unidentate attachment of the N-arylbenzhydroxamate moiety. The

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PMR spectra of trimethylsilyl and dimethylsilyl derivatives show in addition to the ligand peaks a singlet due to methyl group bonded to silicon atom.

Dichlorogermanum bis (N-arylbenzhydroxamates), $(PhCONRO)_2GeCl_2$, have been synthesized by the reaction of germanium tetrachloride with N-arylbenzhydroxamic acid in the presence of triethylamine in benzene.

Attempts to synthesize monoderivatives were futile as it resulted into the formation of the bis products only. The infra-red spectra revealed bidentate mode of attachment of N-arylbenzhydroxamate moiety in these complexes. The presence of two bands in the far IR region assignable to νGe-Cl vibration suggests cis-octahedral geometry (VIII) of the complexes in solid state.

SYNTHESIS OF SOME TRANSITION METAL COMPLEXES OF DITHIOCARBAMATES AND ISOMALEONITRILE DITHIOLATE AND THEIR STRUCTURAL CHARACTERIZATION BY MAGNETIC AND SPECTROSCOPIC METHODS

Mahesh Kumar Singh Sup. *Dr. R. C. Agrawal*

Complexes of Dithiocarbamates

Transition metal complexes of dithiocarbamates have received considerable attention since long because of their relative ease of formation, use as analytical reagents, biocides and more recently as biochemical models and due to varied bonding and stereochemical possibilities presented by them. The literature survey shows that no work has been done on heterobimetallic complexes of dithiocarbamates and their adducts with Lewis bases and on ionic complexes containing complexed cations and complexed dithiocarbamato anions. It was, therefore, thought of interest to undertake synthesis and structural studies of these complexes.

Preparation of the Complexs

The heterobimetallic complexes of the composition $MM'(Dtc)_4$ [M = VO (IV), Mn (II), Fe (II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II) or 2Ag(I); M' = Zn(II), Cd(II) or Hg(II); Dtc = piperidine—or diethyl dithiocarbamate] were prepared by the gradual addi-

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tion of appropriate $M(NO_3)_2$ in acetone-water mixture (4 : 1, v/v) to a solution of Na_2 [M' $(Dtc)_4$] in 1 : 1 molar ratio in the same solvent mixture. The complex salts $Na_2[M'(Dtc)_4]$ required for the preparation of the above complexes, were prepared *in situ* by the gradual addition with vigorous stirring of $M'(NO_3)_2$ solution in acetone-water mixture (4 : 1, v/v) to a solutian of NaDtc in the same solvent mixture in 1 : 4 molar ratio.

The cationic-anionic complexes of the type $[M(L-L)_3]$ $[M'_2(Et_2$ $Dtc)_6]$ [M = Co(II) or Ni(II); M' = Zn(II), Cd(II) or Hg(II); L – L = bipy or o-phen] were prepared by adding gradually a solution of $[M(L-L)_3]$ $[(NO_3)_2]$ in acetone-water mixture (4 : 1, v/v) to a solution of $Na[M'(Et_2$ $Dtc)_3]$ in the same solvent mixture in 1 : 2 molar ratio. The complexes $[M(L-L)$ $][(NO_3)_2]$ and $Na[M'(Et_2Dtc)_3]$, required for the synthesis of the above complexes, were prepared *in situ*. The former complexes were prepared by mixing together acetone-water solution of $M(NO_3)_2$ and L – L in 1 : 3 molar ratio while the latter complexes were obtained by the gradual addition of $M'(NO_3)_2$ dissolved in acetone-water mixture (4 : 1, v/v) to a solution of $NaEt_2Dtc$ in the same solvent mixture in 1 : 3 molar ratio. $Co(Et_2Dtc)_3$ was obtained when attempt was made to prepare $[Co(o-phen)_3]$ $[Hg_2(Et_2Dtc)_6]$ by a similar procedure.

The heterobimetallic and ionic complexes thus prepared have been analysed for metals, nitrogen and sulphur.

All the complexes are insoluble in common organic solvents such as ethanol, acetone, chloroform etc. but slightly soluble in DMF, DMSO or nitrobenzene. They decompose in the temperature range 102-280°C.

The structures of the complexes have been established with the help of molar conductance, magnetic susceptibility, X-ray powder diffraction, electronic, IR and ESR spectral measurements.

Complexes of Isomaleonitrile Dithiolate

The remarkable electronic and structural properties of the 1,2-ethylene dithiolates prompted coordination chemists to investigate the chemistry of 1,1-dithiolate complexes. A variety of transition metal complexes with isomaleonitrile dithiolate (i-MNT) have been synthesized and their properties compared with the complexes of the isomeric 1,2-dicyano-1,2-ethylene dithiolate (MNT).

A careful examination of the literature reveals that no work seems to have been done on 1:1 complexes of Zn(II), Cd(II) and Hg (II) and

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1:2 complexes of Cd(II) and Hg(II) with i-MNT and a very little work has been done on the ternary, cationic-anionic and heterobimetallic complexes of i-MNT with bivalent 3d metal ions. Synthesis and structural studies on the above types of the complexes of i-MNT were, therefore, undertaken.

Preparation of the Complexes

The 1:1 and 1:2 (metal : ligand) complexes of Zn(II), Cd(II) and Hg(II) with i-MNT were prepared by reacting together metal nitrate and K_2i-MNT in 1:1 and 1:2 molar ratios respectively, in aqueous or acetone solution with constant stirring. The ternary complexes of Ni (II) and Cu(II) of the type $M(B)_n$ (i-MNT) were prepared by mixing aqueous solutions of $M(NO_3)_2$ and K_2i-MNT in 1:1 molar ratio in the presence of different molar proportions of the base. The ternary complexes of Zn(II) and Cd(II) containing i-MNT and ethylenediamine (en) were prepared by the reactions of $K_2[M(i\text{-}MNT)_2]$ [M=Cu or Cd (II)] and en taken in different molar ratios in acetone-water mixture.

The complexes thus prepared have been analysed for metals, sulphur and nitrogen.

The structures of the complexes have been studied by the same physico-chemical techniques as employed for dithiocarbamate complexes.

Molar Conductance Studies

The molar conductances of the soluble or slightly soluble ionic complexes in DMSO at 10^{-3}M dilution lie in the range 65 2-85.5 DMF $ohm^{-1}\ cm^2\ mole^{-1}$ indicating their 1 : 1 electrolytic nature. The molar conductivity values of $K_2[M(i\text{-}MNT)_2]$ [M=Zn(II), Cd(II) or Hg(II)] in DMF at 10^{-3}M dilution have been found to lie in the range 118.0—141.6 $ohm^{-1}cm^2mole^{-1}$ showing 2 : 1 electrolytic nature of these complexes. The 2:1 electrolytic nature of the $K_2[Zn(i-MNT)_2]$ is in confirmity with its molecular weight (146.0) determined osmometrically in aqueous solution. All other complexes are non-ionic as shown by the very low values of the molar conductance in DMF or DMSO.

Magnetic Susceptibility Studies

The room temperature magnetic moments of the ternary complexes Ni (bipy/o-phen)$_2$ (i-MNT) (3.20, 2.90 B.M.), Ni(py)$_4$ (i-MNT) (3.20 B.M.) and those of the Co(II) (4.87-4.98 B.M.) and Ni(II) (2.83-3.30 cationic-anionic complexes B.M.) are in accord with spin-free octahedral geometry around the metal ions. The remaining ternary complexes of Ni(II) show subnormal μeff values (1.64-2.39 B.M.)

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which may be due to mixed geometry (square planer + octahedral) around Ni(II). The magnetic moments of Cu(II) complexes indicate the presence of one unpaired electron giving no specific information about their stereochemistry.

Electronic Spectral Studies

The electronic spectra of Co(II) complexes exhibit three d-d transition bands in 9760-10260, 15625-15750 and 20000-23530cm^{-1} regions attributed to transitions $^4T_1g(F) \rightarrow {}^4T_2g(F)$ (ν_1), $^4A_2g(F)$ (ν_2) and ^4T_1g (P) (ν_3) respectively, on the basis of octahedral stereo-chemistry around Co(II).

Infrared Spectral Studies

The ν(C – S) reported to occur in 870-900cm^{-1} region in its transition metal complexes is observed in the same region in the presently studied complexes indicating symmetrical bonding of both the sulphur atoms of i-MNT to metal ion.

X-Ray Diffraction Studies

The prominent lines observed in the X-ray powder diffraction pattern of $K_2[Cd(i\text{-}MNT)_2]$ have been successfully indexed by Ito's method for tetragonal symmetry.

STUDIES ON HETEROCYCLIC COMPOUNDS

Om Prakash Singh Sup. *Dr. Ram Lakhan*

This thesis entitled "Studies on Heterocyclic Compounds" represents an account of investigations carried out by the author on 3-aryl-4-amino-1,2,5-oxadiazoles, 5-aryl-4-amino-1,2,3 (1*H*)-triazoles, 3-phenyl-2-aminoquinoxaline; 6-iodo-2-mercapto-3-aryl (or alkyl)-4(3H)-quinazolinones and their derivatives a antimalarials and CNS active agents; 2-arylimino-3-aryl-5-methyl-4-thiazolidinones, their 1,1-dioxides and 3-aryl-5-methyl-2,4-thiazolidindiones as fungicides, and 2-(*N*-substituted or *N.N*.disubstituted aminoacetamido)-4-arylthiazoles as local anaesthetics.

The recent advancements made in the field of synthetic drugs have drawn the attention of chemists to synthesise new and cheaper compounds of less toxicity and more potency. An extensive work done pre-

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viously on these subjects by several eminent workers gave some useful conclusions on the basis of whieh the present investigations have been carried out.

The thesis has been divided into four chapters depending upon the nature of the work and the type of biological activities associated with the synthesised compounds. All the chapters except first have been sub-divided into four sections : (i) Introduction, (ii) Experimental. (iii) Discussion and (iv) Screening results. Compounds described in chapter I were not subjected to any biological testings and therefore deal only with the chemical aspects.

Chapter—I

This chapter is devoted to explore the potentialities of α - ketonitriles (aroyl cyanides) for the syntheses of various five and six membered heterocycles. Introduction covers some earlier syntheses involving the use of cyanohydrins and α – ketonitriles as synthons under acidic conditions. The author presents here some novel investigations of the reactions of α – ketonitriles with bipolar nucleophiles such as hydroxylamine, hydrazine and *o*-phenylene diamine leading to the syntheses of some five and six membered heterocycles such as 1, 2, 5-oxadiazoles 1, 2, 3 (1*H*)- triazoles and 3-phenyl - 2 - aminoquinoxaline. Literature survey of the known syntheses of these heterocycles are also outlined in the introduction.

Experimental section deals with the syntheses of α – ketonitriles and their reaction with hydroxylamine hydrochloride, hydrate and *o* - phenylene diamine—α – Ketonitriles and hydorxylamine hydrochloride in 1 : 2 molar ratio in absolute ethanol on heating under reflux for 1 - 2 hr in presence of anhydrous sodium acetate afforded 3-aryl-4-amino-1, 2, 5-oxadiazoles. On the other hand, α – ketonitriles react with hydrazine hytrate in absolute ethanol yielding 5 - aryl – 4 – amino – 1,2,3 (1*H*) - triazoles. In an isolated experiment benzoyl cyanide and *o* - phenylene diamine on heating for 1 h in the absence of any solvent produced 3 - phenyl - 2 - aminoquinoxaline. Structural assignments have been carried out on the basis of element analyses, spectroscopic data (IR and NMR) and literature analogies.

The section on results and discnssion deals with the plausible mechanisms for the formation of above heterocycles from α-ketonitriles.

Chapter—II

This chapter is devoted to the study of thioquinazolinone derivatives and divided into four sections. Introduction covers literature on

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the studies of quinazolinones and thioquinazolinones with their structural modification and medicinal utility.

Experimental section deals with the synthesis of 6-iodo-2-mercapto-3-aryl (or alkyl)-4 (3H)-quinazolinones and their 2-(*N*,*N*-dialkylaminoethyl) thio derivatives. These compounds have been synthesised by the reaction of 5-iodoanthranilic acid with aryl (or alkyl) isothiocyanates in absolute ethanol followed by S-alkylation of the resulting 6-iodo-2-mercapto-3-aryl (or alkyl)-4(3H)-quinazolinones with halogen compounds (prepared from *N*-substituted and *N*,*N*-disubstituted β-aminoethanols and 48% hydrobromic acid and isolated as bromide hydrobromide salts) in alcoholic alkaline solution. The physical and IR spectral data of the 6-iodo-2-(β-substituted aminoethyl) thyo-3-aryl (or alkyl)-4(3H)-quinazolinones are given in Tables 2-6.

The section on discussion is further divided into two parts. (A) In this section reaction conditions for obtaining good yields of different isothiocyanates and thioquinazollnones are discussed. It has been proved that the alkylation of thioquinazolinones occurs at the sulphur atom at position 2 rather than the nitrogen atom at position 1. (B) NMR and IR spectroscopy in structural studies : This part deals with the establishment of the structures of the synthesised compounds.

The fourth section gives an account of the screening results (Tables 7 and 8) of some selected quinazolinones. The compounds have been screened for their antimalarial and CNS activity at the National Institute of Communicable Diseases, Delhi and Central Drug Research Institute, Lucknow, respectively.

Chapter—III

This chapter is also divided into four sections. Introduction deals with the historical approaches made by previous workers to the syntheses and biological activities of 4-thiazolidinone and 2,4-thiazolidindione derivatives.

In the experimental section, syntheses of 2-arylimino-3-aryl-5-methyl-4-thiazolidinones is described. Symmetrical *N*,*N*'-*bis*-(disubstituted) arylthioureas have been prepared from disubstituted anilines and carbon disulphide by oxidation with iodine in pyridine solution. These thioureas on condensation with 2-bromopropionic acid or ethyl 2-bromopropionate in the presence of either fused sodium acetate or pyridine in absolute ethanol yield the corresponding 4-thiazolidinones. A couple of 4-thiazolidinones were oxidised with potassium permanganate in acetic acid solution to yield the corresponding 1,1-dioxides.

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All the 4-thiazolidinones except one were hydrolysed with strong HCl in ethanolic or acetic acid medium to give the related 3-aryl-5-methyl-2, 4-thiazolidindiones. The characterisation and IR spectral data of compounds are recorded in Tables 1-5.

In the third section optimum conditions for the reaction have been discussed. The mechanism of the formation of products is also given.

Section four describes the fungicidal activity of 2-arylimin-3-aryl-5-methyl-4-thiazolidinones and 3-aryl-5-methyl-2,4-thiazolidindines. Food poisoning method has been adopted for the screening of compounds using *Trichoderma viride* and *Curvularia lunata* as the test fungi. The results are summarised in Table 6. Some of the compounds are observed to be more potent than a commercially used fungicide 'cuman'.

Chapter—IV

A study of 2-(*N*-substituted or *N*,*N*-disubstituted aminoacetamido)-4-arylthiazoles as local anaesthetics is presented in this chapter. Introduction gives an account of the earlier work done on local anaesthetic compounds with their structural modifications.

In the experimental section, the synthesis of 2-(*N*-substituted or *N*,*N*-disubstituted aminoacetamido)-4-arylthiazoles is described. 2-Chloroacetamido-4-arylthiazoles, obtained from the reaction of 2-amino-4-arylthiazoles with chloracetyl chloride, are converted into 2-(*N*-substituted or *N*,*N*-disubstituted aminoacetamido)-4-arylthiazoles by treatment with different primary and secondary amines in ethanol in presence of potassium carbonate. The hydrochlorides of the bases have been prepared as usual. The physical data of the above compounds are listed in Tables 1 and 2 while the spectral data in Tables 3 and 4.

The third section deals with discussion of the optimum reaction conditions for obtaining good yield of the products. The mechanism of the reaction are also given.

In the fourth section, local anaesthetic activity results of the hydrochlorides have been summarised (Table 5). Frog's sciatic plexus method has been employed for screening the compounds for conduction anaesthesia. The results have been compared with that of standard local anaesthetic procaine.

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STUDIES ON ION-SOLVENT INTERACTIONS IN ELECTROLYTE SOLUTIONS IN N, N-DIMETHYLFORMAMIDE-WATER MIXTURES THROUGH VISCOSITY MEASUREMENTS

Raj Deo Singh Sup. *Dr. P. K. Tikkoo*

The present dissertation comprises mainly the results of the author's work on the viscosity measurements of some alkali halides and quaternary ammonium bromides in N, N-dimethylformamide (DMF)-water mixtures at different temperatures in moderately dilute region. The dissertation is divided into six chapters. Chapter I comprises the "Introduction" which deals with a brief review of the history, theory and devement of the subject under investigation. The purpose of the present work is given under the heading "Statement of the problem" in Chapter II. The centre of study being the study of ion-solvent interactions through viscosity measurements, various types of electrolytes, viz., potassium chloride, bromide and iodide, lithium, sodium, caesium, tetramethyl ammonium tetraethyl ammonium and tetrabutylammonium bromides have been critically examined regarding their viscosity behaviour in DMF-water mixtures at different temperatures. Experimental techniques employed for the measurements of viscosity and density have been described in Chapter III. Chapter IV contains the results of the present investigation and in Chapter V the discussion of the results mainly in terms of the B-coefficient, and thermodynamic activation parameters has been presented. This is followed by Chapter VI under the heading "Summary' in which the findings of the present work are concluded in brief. Finally, a consolidated list of references and the various books consulted is given. The thesis ends with appendices in which the published papers are presented.

The viscosity measurements were made using a calibrated uhelohde viscometer with a viscometer constant 0.003910 centistokes/sec. A calibrated pyknometer of about 15 ml capacity was used for density measurements. The experimental temperatures were maintained using water thermostat with an accuracy of $\pm 0.01^{\circ}C$.

The experimental data have been analysed using Jones-Dole equation ($\eta/\eta^{\circ} = 1 + Ac_{\frac{1}{2}} + Bc$). The coefficient A and B have been determined by least square fitting on ICL1900 computer. The activation parameters such as free energy, enthalpy and eutropy of activation for viscous flow have been calculated from viscosity data, B-coefficients at different temperatures and molar volumes. These parameters alongwith

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the temperature coefficient of viscosity B-coefficient and concentration gradient of viscosity have been utilized to interpret the observed results with respect to solvent-solvent and ion-solvent interactions.

The DMF-water mixtures used as solvent show interesting variation in their viscosities and first derivatives of viscosity as a function of solvent composition. The viscosity of the solvent mixture at all the experimental temperatures increases rapidly with increase in DMF content reaching to a maximum corresponding to the solvent composition containing about 0.28 mol fraction DMF and decreases thereafter with a comparatively slower rate. The existence of the maximum in viscosity corresponding to the mixed solvent containing 0.28 mol fraction of DMF indicates strong structure formation between water and DMF molecules and is attributed to the formation of the solvated complex 2DMF. $5H_2O$.

The nature of viscosity B-coefficient versus solvent composition curves reveal that in the case of predominantly structure-forming electrolyter, possessing high positive B-values in aqueous solutions (eg. LiBr, NaBr and Et_4NBr) as well as structure-breaking electrolytes, possessing negative or very small positive B-values in aqueous solutions (e. g. KBr, KI, CsBr and Me_4NBr), the values of B-coefficient first diminish and then increase after attaining minima at about 0.06, 0.04, 0.02 and 0.01 mol fractions DMF at 25°, 30°, 35° and 40°C respectively. The solvent compositions corresponding to minimum in B-values indicate the region of maximum structuredness of the solvent at these temperatures. The term structuredness used above relates to the compactness of the solvent system rather than to complex formation only. Thus, in water-rich region of the solvent mixture, the addition of small amount of DMF to water results in a more structured solvent as indicated by B-minima.

The change in free energy of activation for viscous flow due to addition of electrolytes in solvent mixtures ($\Delta\bar{G}_2^{o\ddagger} - \Delta\bar{G}_1^{o\ddagger}$) also shows a minimum with change in solvent composition for all electrolytes studies except for KCl. In case of negative values of ($\Delta\bar{G}_2^{o\ddagger}$) obtained for structure-breaking electrolytes, the minimum corresponds to the maximum contribution of electrolyte leading to maximum disruption of solvent structure by these electrolytes, which is obvious in the most structured solvent. On the other hand, for electrolytes having positive ($\Delta\bar{G}_2^{o\ddagger} - \Delta\bar{G}_1^{o\ddagger}$) values the minimum corresponds to the least contri-

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bution of electrolytes which indicates least structure formation in the mixed solvent. Negative and positive changes in free energy of activation for viscous flow due to addition of electrolytes in mixed solvent indicate their structure-breaking and forming properties, respectively.

On the basis of above arguments, it can be said that the minima in the plots of $(\Delta\bar{G}_2^{o\ddagger} - \Delta\bar{G}_1^{o\ddagger})$ vs. x (mol fraction DMF) correspond to the maximum breaking or least formation of the solvent structure depending upon the negative or positive $(\Delta\bar{G}_2^{o\ddagger} - \Delta\bar{G}_1^{o\ddagger})$ values in water-rich region. Hence, it was concluded that the most structured solvents are the solvent mixtures containing 0.06, 0.04, 0.02 and 0.01 mol fractions DMF at 25°, 30°, 35° and 40°C respectively. Enthalpy and entropy of activation for viscous flow of electrolyte solutions also indicate the structured region of the mixed solvent. These conclusions are well in agreement with those concluded on the basis of B-minima as well as Frank's treatment, according to which the region of the maximum in $d\eta/dx$ vs x indicates the structured solvent. Further, the minimum in $d\eta/dx$ vs. x and dB/dT equal to zero for electrolytes were obtained at about the same solvent composition, i.e., 0 50 mol fraction DMF showing the mixed solvent to be the least structured at this composition.

STUDIES ON SOME FIRST ROW TRANSITION METAL COMPLEXES OF *N*-ETHOXYTHIOCARBONYL HYDRAZIDE AND ITS N¹-SUBSTITUTED DERIVATIVES

Suresh Chandra Srivastava Sup. : *Dr. N. K. Singh*

Transition metal complexes of the ligands containing nitrogen and sulphur as donors have been less extensively studie as compared to those of nitrogen and oxygen donors. Ligands containing sulphur-nitrogen, Sulpher-oxygen-nitrogen as potential donors in metal complexes have also been studied in some detail. These ligands comprises of pyridine-thiols, aminothio β-diketones, thiosemicarbazides, thiocarbohydrazides, thiohydrazides, dithiocarbazates and their derivatives with carbonyl compounds. Thiosemicarbazide (Htsc) is one of the simplest representative of ligands having nitrogen and sulphur as donors and the complexing ability of Htsc have been studied. Complexes of a number of thiosemi-

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carbazones of aliphatic and aromatic aldehydes and ketones with various transition metal ions have also been synthesised and characterized. The complexing ability of thiohydrazides, R—CSNHNHR' (R = Ph; R' = H, CH_3, Ph, PhCO, $CONH_2$, $CSNH_2$) and thiohydrazones with various transition metal ions are reported in literature; and the complexes are generally analogous to those of thiosemicarbazides and thiosemicarbazones.

A number of thiosemicarbazides, thiosemicarbazones, thiohydrazides and thiohydrazones, and some of their metal complexes have been found to be biologically active in several ways, and it was shown that few free ligands and their metal complexes are antibacterial, fungistatic, as well as active against small pox, virus diseases and certain kinds of tumor.

The introductory chapter encompasses the literature survey on the complexes of dithiocarbazates, thiosemicarbazides, thiohydrazides and their derivatives, as these ligauds have a common thiohydrazide moiety present in ethoxythiocarbonyl hydrazide and its *N*'—substituted derivatives.

In view of the absence of the previous work on the 3d metal complexes of ethoxythiocarbonyl hydrazide (Heth), acetylacetoneethoxythiocarbonyl hydrazone (H_2acac eth), salicylaldehyde ethoxythiocarbonyl hydrazone (H_2L), N, N'-*bis* (ethoxythiocarbonyl) hydrazine (H_2deth), N'-ethoxycarbonyl-N^2-ethoxythiocarbonyl hydrazine (H_2eceth), N^2-ethoxythiocarbonyl benzoic acid hydrazide (H_2etbh) and N^2-ethoxythiocarbonyl pyridine-4-carboxylic acid hydrazide (H_2etph), it was thought of interest to undertake a systematic preparative and structural studies of these complexes.

Preparation of the complexes

The adducts have generally been prepared by mixing the ethanolic solutions of the appropriate metal(II) chloride and the ligand (Heth. HCl) was used for the preparation of the adducts of Heth) in ~1 : 2 or 1 : 3 molar ratio, and stirring the reaction mixture.

$[Co(Heth)_3]Cl_3$ was however, obtained by the addition of few drops of dil. HCl to the reaction mixture. The adduct of Fe(II) chloride have been prepared under nitrogen atmosphere to prevent the oxidation.

1 : 2 deprotonated complexes of Heth and H_2L have been prepared by mixing ethanolic solutions of respective metal(II) chloride and the corresponding ligand in ~ 1 : 2 molar ratio and adding two equivalents

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of ethanolic KOH in the case of Fe(II) and $Ni(eth)_2$ (light-yellow compound), and raising the pH to ~ 5-6 with dil. NH_4OH in others. Whereas, the 1 : 2 deprotonated complexes of H_2etbh and H_2etph were prepared by adding aqueous solutions of the respective metal(II) acetate to the ethanolic solution of the ligands in 1 : 2 molar ratio and then adding some sodium acetate to the above reaction mixture. 1 : 2 or 1 : 1 deprotonated complexes of Fe(II) were prepared by mixing ethanolic solutions of $FeCl_2$. $4H_2O$ and the respective ligands in appropriate molar ratio and then adding required amount of ethanolic solution of KOH.

1 : 1 deprotonated complexes were prepared by mixing together ethanolic/aqueous solutions of corresponding metal(II) acetate/chloride and the ethanolic solution of the ligands in 1 : 1 molar ratio followed by the addition of eq, sodium acetate in all cases, except Mn(acaceth) H_2O, Mn(deth) and Mn(eceth) where a few drops of dil. NH_4OH were added.

The 1 : 2 and 1 : 1 deprotonated complexes thus precipitated were digested on water bath for few minutes.

$VOL.2H_2O$ and Co(HL) (L) were prepared by mixing the ethanolic solutions of the ligand and hydrated vanadyl/cobaltous chloride in 1 : 2 molar ratio and stirring the reaction xmiture. $NiL.NH_3$ was obtained by adding concentrated ammonia solution dropwise to the ethanolic solution of $NiCl_2$. $6H_2O$ and H_2L in 1 : 1 molar ratio till present in alight excess and concentrating the reaction mixture to incipient crystallisation. [$Ni(eth)_2$acacH] was prepared by refluxing a suspension of $Ni(eth)_2$ in ethanol with acetylacetone (~ 1 : 5 molar ratio) for ~ 4 hours.

The complexes thus precipitated were suction-filtered, washed with ethanol/water and dried *in vacuo*.

The complexes have been analysed for their metal, chloride, hydrazine and sulphur contents using standard literature procedures and nitrogen by microanalysis.

The structure of the complexes have been established with the help of molar conductance, magnetic susceptibility, electronic, IR, X-ray powder diffraction and ESR spectral measurements.

Magnetic susceptibility studies

Diamagnetic nature of $Co(Heth)_3Cl_3$ and Co(HL) (L) show that these complexes are low-spin octahedral. All Co(II) complexes have their magnetic moment values (μ_{eff} 4.20-4.56 B. M.), which fall well within the range of tetrahedral coordination around Co(II). An octahe-

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dral geometry is suggested from the observed magnetic moment of 3.15-3.60 B. M. for $[Ni(Neth)_3]Cl_2$, $Ni(H_2L)Cl_2.2H_2O$, $Ni(HL)_2$ and $Ni(Hetph)_2$. The magnetic moments of 1.53 and 2.0 B. M. for $Ni(eth)_2$ (light yellow complex) and Ni(eceth) respectively may be explained by assuming a mixed stereochemistry (square-planar+tetrahedral) around Ni(II). The diamagnetism of other Ni(II) deprotonated complexes suggest their square-planar geometry.

Electronic spectral studies

The electronic spectrum of $VOL.2H_2O$ shows two bands at 10,000 and 18180 cm^{-1} assigned to $d_{xy} \cdot d_{yz}$; d_{xz} and d_{x2-y2} transitions, respectively on the basis of octahedral geometry.

The visible region spectra of $Fe(eth)_2.2H_2O$, Fe(deth). $2H_2O$, Fe (eceth) $.2H_2O$, $Fe(etbh)_2$ and $Fe(etph)_2$ show one broad band in the 10250-15300 cm^{-1} region assigned to $^5T_{2g} \rightarrow {}^5Eg(D)$ transition in the octahedral environment of the metal ion.

The spectra of $Fe(H_2L)Cl_2$, $Fe(HL)_2$, $Fe(etbh)_2$ and $Fe(etph)_2$ yield one bond in the 17390-22200 cm^{-1} region, which may be attributed to charge transfer transition $t_{2g} \rightarrow \pi^*$.

Infrared spectral studies

The bonding sites of the ethoxythiocarbonyl hydrazide and its *N'*-substituted derivatives involved in their transition metal complexes have been determined from a careful comparison of the infrared spectra of the complexes in nujol with chloroform solution spectra of the parent ligands.

ESR spectral studies

The ESR spectra of $Cu(acaceth).H_2O$, $Cu(H_2L)_2Cl_2$ and $CuL.H_2O$ in solution are isotropic at room temperature and nearly axially symmetric at 77°K, while those of Cu(etbh) and Cu(etph) are characteristic-of axial symmetry in the solid state. The trend $g_{11} > g\perp > ge$ (2.0023; spin-free value) indicate that the unpaired electron is most likely in d_{x2-y2} orbital of Cu(II).

^1H NMR

^1H NMR spectrum of H_2 acaceth in CCl_4 indicates the presence of keto-enol form of the ligand in solution, whereas that of ZnL. EtOH in DMSO(d_6) indicates the presence of coordinated ethanol.

Antifungal activity

Antifungal activity of the complexes suggest that $[Co(Heth)_3]Cl_3$ is relatively more fungitoxic than $[Ni(Heth)_3]Cl_2$ and $Cu(Heth)Cl_2$. Further, the Co(II) and Ni(II) complexes of H_2deth and N_2eceth are better antifungal agents than their corresponding free ligands.

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GEOGRAPHY

सकलडीहा विकास खण्ड (जनपद वाराणसी) का समन्वित ग्रामीण क्षेत्रीय विकास एवं नियोजन : एक भौगोलिक अध्ययन

कृष्ण कुमार सिंह

निर्देशक : डा० डी० एन० सिंह

देश की विद्यमान आर्थिक, सामाजिक एवं राजनैतिक स्थिति में ग्रामीण विकास की अनिवार्यता निर्विवाद है। भारतीय अर्थतन्त्र की द्विधात्मक प्रादेशिक संरचना, जो प्रमुखतः औपनिवेशिक काल की विरासत है, निश्चित रूप से स्वतन्त्रोत्तर काल में प्रखर हुयी है। इसका एक मुख्य कारण भारतीय कृषि अर्थव्यवस्था एवं गाँवों का पिछड़ापन तथा उन पर समुचित ध्यान का अभाव है। यह स्थापित सत्य है कि औद्योगिकीकरण के बावजूद भी गाँवों एवं उनकी समस्याओं का बुनियादी महत्व बना हुआ है। वर्तमान सन्दर्भ में शुद्ध उत्पादन एवं तदर्थ भारी उद्योगों के संश्लिष्ट-निर्माण पर बल देने वाले नियोजकों द्वारा भी ग्रामीण विकास की समीचीनता एवम् अनिवार्यता को बाध्य रूप से स्वीकार करना इस बात का स्पष्ट प्रमाण है। देश में, गाँवों के विकास के उद्देश्य स्वरूप समय-समय पर अनेक विकास योजनायें चलायी गयी, परन्तु इनसे अभिलक्षित परिणाम की प्राप्ति न हो सकी। वस्तुतः यह अनुभव किया गया कि असफलता का मूल कारण विकास कार्यक्रमों की प्रायः एक दूसरे से असम्बद्धता है। अतः इस तथ्य को ध्यान में रखते हुए विभिन्न कार्यक्रमों में समन्वयन पर बल दिया गया तथा एक बृहद् विकास कार्यक्रम के अन्तर्गत समन्वित ग्रामीण विकास कार्यक्रम प्रस्तुत किया गया। प्रस्तुत शोध-प्रबन्ध इसी परिप्रेक्ष्य में तैयार किया गया है। यह क्षेत्र मध्य गंगा घाटी में स्थित जनपद वाराणसी के चन्दौली तहसील का एक विकासोन्मुख विकास-खण्ड है। इसका आक्षांशीय विस्तार 25° 15′ उत्तर से 25° 30′ उत्तरी तथा देशान्तरीय विस्तार 83° 8′ पूर्वी से 83° 22′ पूर्वी है। तदनुसार इसका कुल क्षेत्रफल 21627.92 हेक्टेयर एवं जनसंख्या 135796 ‡1981‡ है। विकास खण्ड में कुल 180 ग्राम हैं जिनमें 22 ग्राम जनविहीन हैं।

प्रस्तुत शोध-प्रबन्ध की रूपरेखा का निरूपण 8 अध्यायों के माध्यम से किया गया है। प्रथम अध्याय सैद्धान्तिक पृष्ठभूमि से सम्बन्धित है, जिसके अन्तर्गत समन्वित ग्रामीण विकास की अवधारणा, अभिप्राय एवम् उद्देश्य तथा इसके ऐतिहासिक संदर्श का विवेचन किया गया है। शोध-प्रबन्ध का संगठनात्मक प्रारूप भी इसी अध्याय के अन्त में प्रस्तुत है। अध्याय द्वितीय एवं तृतीय में क्रमशः क्षेत्र विशेष का भौगोलिक वैशिष्ट्य एवं वहाँ विद्यमान विविध प्राकृतिक एवम् सांस्कृतिक संसाधनों के ज्ञात एवं सम्भाव्य स्वरूप तथा उनके उपयोग प्रतिरूप का विश्लेषण किया गया है। इस प्रकार विविध संसाधनों के वर्तमान उपयोग में निहित त्रुटियों के आधार पर अनुकूलतम उपयोग हेतु सुझाव प्रस्तुत किये जा सके हैं। चतुर्थ अध्याय कार्यात्मक-भूवैन्या-

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सिक संगठन के सन्दर्भ में अधिवास प्रतिरूप, कार्य एवम् उनके पदानुक्रम, सेवा केन्द्रों का निर्धारण उनकी पदानुक्रमिक व्यवस्था आदि पक्षों का विवेचन है। यहाँ स्थानिक एवम् कार्यिक अन्तराल के आधार पर विभिन्न स्तर के नये सेवा केन्द्रों के प्रतिस्थापन का सुझाव दिया गया है। अध्याय पाँच में कृषि एवम् तत्सम्बन्धित सहकार्यों के विद्यमान स्वरूप की समालोचना तथा उनके विकास हेतु नियोजन की रूपरेखा प्रस्तुत है। इसमें निम्न कृषि-उत्पादकता तथा उसके कारणों पर प्रकाश डालते हुये कृषि अवस्थापना तत्वों एवम् वांछित कृषि सहसम्बन्धी क्रिया-कलापों के समुचित विकास पर बल दिया गया है। षष्टम् अध्याय में क्षेत्र के स्थानीय संसाधनों एवम् सामाजिक-आर्थिक ररिस्थितियों को देखते हुए औद्योगिक विकास हेतु योजना प्रस्तावित की गयी है। सामाजिक आर्थिक सेवाओं, जो मानव जीवनयापन के ढंग को सुधारने तथा उसके स्तर को ऊँचा करने के लिए अनिवार्य मानी गयी हैं, की भूवैन्यासिक संरचना की व्याख्या एवम् उनका उचित समायोजन सप्तम् अध्याय की विषय-वस्तु है। अष्टम अध्याय में सारांश रूप में सम्यक् तथा समन्वित क्षेत्रीय ग्रामीण विकास हेतु नियोजन की रूपरेखा तैयार की गयी है। इसके अन्तर्गत विकास के विविध अवयवों, जिनका कई अध्यायों में अलग-अलग विश्लेषण एवं तदनुसार नियोजन प्रस्तावित है. को एक समन्वित परिप्रेक्ष्य में रखकर पुनरावलोकन किया गया है। इस सम्बन्ध में नीति निर्माण प्रक्रिया के दोषों को बतलाते हुए भ्रष्टाचार के प्रतिरोधात्मक प्रभाव को स्पष्ट रूप से अंकित किया गया है। विकास प्रक्रिया में समायोजन एवम् समन्वीकरण को ध्यानस्थ करके अध्ययन क्षेत्र के सर्वांगीण विकास हेतु यथासम्भव प्रयोगात्मक सुझाव प्रस्तुत किये गये हैं।

यहाँ पर यह बताना समीचीन होगा कि विभिन्न अध्यायों में उचित स्थान पर सम्बन्धित विकास प्रक्रिया को स्पष्ट करने का प्रयास किया गया है तथा सुझाव प्रस्तुत करते समय यथासम्भव उनके क्षेत्र के सन्दर्भ में प्रयोगात्मकता पर ध्यान दिया गया है। उदाहरणार्थ, उद्योग तथा तकनीक के प्रकार एवम् स्तर का निर्धारण विद्यमान क्षेत्रीय संसाधनों एवम् विकास स्तर को दृष्टिगत रखकर किया गया है। आधुनिक समय में प्रचलित सांख्यिकीय प्रविधियाँ समुचित परीक्षण के पश्चात् उपयोग में लायी गयी हैं। इस सन्दर्भ में आँकड़ों से सम्बन्धित सीमितताओं पर भी विचार किया गया है।

शोध-प्रबन्ध के अन्त में अध्ययन का सारांश एवम् निष्कर्ष दिया गया है जिससे पाठक एक विहंगम दृष्टि में अपने को क्षेत्र की प्रमुख विशिष्टताओं से परिचित करा सके।

GEOHYDROLOGY AND GROUNDWATER RESOURCES OF BULANDSHAHR DISTRICT : A GEOGRAPHICAL STUDY

Bharat Bhushan Jain Sup. : *Dr. R. N. Mathur*

The work presents the results of a detailed study of Groundwater Resources and Geohydrology of Bulandshahr district (4288.06 km), occupies a central position in the Upper Ganga-Yamuna Doab and

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thus represents the whole region. The conclusions arrived at, will thus be approximately applicable to the whole region.

Bulandshahr district is characterised by moderate subtropical monsoon climate and is almost a flat surface, formed out of unconsolidated alluvial deposits, sloping imperceptibly from north-west to south-east at a gradient of 1 in 2,500.

The geohydrological conditions of the area have been studied from the logs of tubewells bored in the area. The finer material, especially clay, predominates at shallow depths (up to 10 m below the ground) whereas the coarser materials, generally forming an aquifer, predominate at greater depths (up to 120 m below ground). There is a marked tendency towards an increase in the total thickness of aquifers from west to east.

Rainfall, being the main source of groundwater recharge in the area, shows a slightly increasing tendency from south-east to north-west. Further, there is no definite periodicity of heavy or low rainfall years during the 80-year period of record. A climatological water surplus is recorded only in a heavy rainfall year and that too only in the months of August and September, bringing in sharp focus the significance of irrigation in this predominantly agricultural area.

The characteristic features of water table, the spatial variations in the water table depths although of a minor nature, do clearly reflect some variations in the surface relief. Thus water table depths increase away from the interfluves, approximately marked by the courses of the three main canals. Water table depths over the district range between 3 to 12 m. Well hydrographs of different selected areas, indicate that the groundwater level is mainly influenced by local rainfall. The fluctuations due to tubewell pumping in a heavy and normal years are only of a +1.09 and +0.09 m and they are, in fact, just superimposed on the usual fluctuations due to variations in local rainfall amounts.

The total groundwater potential in the area has been assessed on the basis of available water bearing strata, which amounts 2,681,657 ha m. In the area groundwater recharge occurs by influent seepage from rainfall, surface water bodies, irrigated fields and by groundwater inflow which amounts to 156,807.58 ha m. Groundwater discharge occurs by evaporation and transpiration, effluent seepage into surface water bodies, groundwater outflow and by pumping from wells which amounts to only 82,339.41 ha m. There is a balance of 74,468.17 ha m for further exploitation in the district.

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Safe yield is the amount of groundwater which can be withdrawn annually from a groundwater basin without producing any adverse effect. It has been taken to be the amount of ground water recharge in a heavy rainfall year, for instance, in 1975 it was 150,787.43 ha m.

The chemical quality of wells in the area is found good to moderately good for irrigation. However, there are some pockets, mostly located near Banjurpur and Khurja, where the groundwater is highly saline and can be used to irrigate only salt tolerant crops which are barely, sugarcane, tobacco, mustard, cotton etc. The total hardness in the groundwater is high but does not make it unfit for domestic use.

The development of surface water resources for irrigation has attained their maximum by the year 1950. In the study area over increasing demand of water for irrigation has resulted in a large scale development of groundwater resources. The groundwater consumed in different uses are : rural water supply-2.90%, urban and industrial-0.92% and irrigation-96.18%. The large-scale utilization started only from 1950 with the introduction of tubewells in the area. As regards the % share of different types of wells in the District, the figures for 1980 are : PTW-63.8, STW-12.6, PS-9.3, PW-6.4 and MW-7.8%. The intensity of pumping is highest in the case of PTW 30.827 ha m/km^2 followed by MW 8.24 ha m/km^2, STW 4.188 and PS 0.306 ha m/km^2. Blockwise intensity of pumping, taking into account all types of wells together is highest in Unchagaon (48.05 ha m/km^2) and lowest in Khurja (21.98 ha m/km^2). As regards the intensity of pumping over the District as a whole, it has increased from 18.70 in 1960 to 31.90 ha m/km^2 in 1980. The net area irrigated has shown a corresponding increase from 34.80% of the net area sown in 1960 to 52.7% in 1980.

Four factors, namely land consolidation, rural electrification, institutional credit and advent of HYV seeds are widely believed to have improved private profitability of investment in an individually-owned PTW. Whereas the temporal progress in the first three factors has been gradual overtime, the improvement in on-farm benefits from groundwater irrigation was essentially a one-shot occurence with the HYV revolution in the study area's agriculture.

On the other hand groundwater utilization in the non-agricultural sector has increased by 104.68 % from 1960 to 1980 and it amounts to 3.82% of the total groundwater pumped in 1980. There has been a marked increase in the rate of utilization for domestic and municipal purposes which is obviously due to the increasing pressure of population

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In the study area the consumption of groundwater in the urban centres has been estimated to be 65 litres per capita per day (lpcd) whereas for the rural population it is 30 litres. In 1980 only 15% of the villages were served with protected water supply, 65% of the villages got the drinking water from open masonry wells, 10% from rivers, lakes. and springs, 8% from tubewells and the rest from tanks, ponds and other sundry sources.

The study area is generally free from the different problems often arising in the course of utilization of groundwater, for example water logging, water pollution, soil salinityt and alkalinity and water table decline due to pumping.

The areas of under utilization, balanced-utilization and overutilization have been delineated and water requirements by 2001 A. D. have been estimated on the basis of average rate of growth in population and in the different sectors of the economy.

Suggestions for implementation of conservation practices have been put forward so as to reduce the total overutilization of 7,071.68 ha m in blocks where the safe limit has already been crossed (Anupshahr, Bawan Bahadur Nagar, Danpur, Siyana, Unchagaon and Shikarpur) or where it is likely to be crossed in the near future (Pahasu, Gulaothi, Debai and Jahangirabad).

Suggestions have also been put forward for stoppage of wasteful expenditure of water and for increasing irrigation efficiency by adopting the various conservation methods for example, moisture conservation in unirrigated areas, proper tillage practices, proper crop planning, checking seepage from irrigation channels, conjunctive use of surface water with saline groundwater, etc. A planned utilization of groundwater resources of the area will undoubtedly lead to an integrated economic development of the area.

The additional number of works to be constructed for meeting the unutilized potential have been worked out as : STW-1, 215, PTW-6, 580 and PS-7, 90, keeping in view the present trend and the future possibilities.

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HIMALAYAN RAMGANGA BASIN : A GEOMORPHIC STUDY

Vibhash Chandra Jha Sup. : *Dr. N. K. P. Sinha*

The present study is an attempt to analyse the drainage, landform and other morphometric attributes of the Himalayan Ramganga basin with a view to trace the stages in its evolution, It is divided into 7 chapters, namely (1) Introduction. (2) Geologic and Tectonic Background, (3) Climate and Geomorphic Processes, (4) Relief and Drainage, (5) Basin Morphometry, (6) Terrain Morphology, and (7) Morphological Evolution of the Himalayan Ramganga Basin.

The Himalayan Ramganga (29°29′ 56″N-30°06′24″N; 78°36′00″ E-79°34′30″E) is a basin of 8th order, covering parts of the Lesser Himalayas and the Siwaliks in Uttar Pradesh, and administratively includes portions of the districts of Pauri, Chamoli, Almora and Nainital. Its catchment area measures 3,134 km² and the basin elevation varies from 269 m (Kalagarh) to 3,098 m (Kotiabagar). The trunk stream, which is fed by 35 important tributaries, has a total length of 158 km.

Analysis of absolute relief reveals that about 22.6% of the basin-area lies in the altitudinal zone of 1,200 m-1,500 m, mostly located in the central and northwestern parts of the basin. The other height categories of less than 600 m, 600 m-900m, 900 m-1,200 m, 1,500 m-1,800 m, 1,800 m-2,100 m and over 2,100 m account for about 11.0%, 14.3%, 20,1%, 15.2%, 9.9%, and 6.9% of the basin area respectiveley.

Presence of 16 geological formations, ranging in age from Pre-Cambrian to Pleistocene and Recent times, have been noted with their lithologic attributes. Tectonically, the south-western half of the basin has been greatly affected by more recent structural movements, including the formation of Lansdowne synclinorium and the Main Boundary Fault. Occurrence of four major and two minor faults of earlier times have been also noted in the northeastern half of the basin.

Climatically the area experiences a milder summer and a much colder winter than the plains to the south. Variation in the amount of rainfall accounts for variation in the character and intensity of operation of geomorphic processes, which very greatly from the forest-covered lower altitudinal zones to sparsely vegetated higher altitudinal zones. In general, the basin lies in the moderate morphogenetic region with maximum impact of fluvial erosion.

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The absolute relief of 1,000 m-1,750 m characterizes 50% of the basin-area. Similarly, about 78% of it has high to very high relative relief. Moderate to moderately high relative relief characterizes about 17% of the basin. Low relative relief, associated with the valley bottom of the Lesser Ramganga, accounts for the remaining 5% of the area.

About 62.8% of the basin is characterized by high dissection index. High to very high and very low to low dissection indices characterizes 5.3% and 31.9% of the basin-area.

The basin, which has been divided into 8 physiographic regions, exhibits 5 different types of drainage patterns, including dendritic, radial, parallel, rectangular and trellis.

A detailed quantitative analysis of 35 tributary basins, including 1 of seventh order, 5 of sixth order, 10 of fifth order, 16 of fourth order and 3 of third order, has been presented. It includes analyses of stream order, number, mean stream-length, bifurcation ratio, stream-length ratio, relief ratio, elongation ratio, circularity ratio, valley-side and channel slopes (of 15 tributary basins only), sinuosity index, drainage density and stream frequency, and hypsometric curves. Calculation of hypsometric integral reveals that the trunk stream Ramganga (38.25%) is in late mature stage of its development. Its 2 tributary streams are in early youth, 5 in late youth, 14 in early mature, 7 in middle mature and the remaining 7 in late mature stages of development. The morphology of the basin has been studied with the help of average alopes and serial profiles (N-S and E-W). Existence of four prominent levels of regional terraces have been noted. After examining the various morphometric attributes, the basin has been classified into 2 first-order, 9 second-order, 37 third-order and 48 fourth-order morpho-units.

Among the important landforms found in the basin are primary mountain ranges and flat-topped uplands, gorges and narrow 'V'-shaped valleys, floodplains, entrenched meanders with interlocking spurs, free-face, debris slope and talus deposits associated with fault-line scarps, and convex-sloped laccolithic mountains.

Thus, it has been possible to identify the following stages in the evolution of the Ramganga basin :

(1) The basin formed a part of Tethys geosyncline until the Pre-Tertiary times. Successive upliftments of the area in Eocene-Oligocene times resulted in the formation of a NW-SE mountain range (forming part of the Lesser Himalayas), on which the Ramgagga first developed

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as a south-flowing consequent stream and later cut its gorge in the upper valley tract. Its major tributaries such as the Siuni, Khansar and Bimoli Gadhera were also established in this period.

(2) Formation of Lohba-Dwarahat thrust (trending NNW-SSE) in Mid-Oligocene times not only resulted in the bifurcation of the main mountain range into two parts, namely the Dudhatoli Ki Dhar and the Khankrakhet Ki Dhar, but also in the development of the Kuthrar and Khastari Gadhera, the two fault-guided tributaries of the Ramganga in the north-central part of the basin. The simultaneons development of Lansdowne and Bhikhiasain thrusts in the western and central parts resulted in the growth of tributaries like the Mandalti, Mandal, Deota, Nair and Binau.

(3) Formation of the Main Boundary Fault in End-Oligocene times changed the former southerly course of the Mandal to its present south-easterly course, meeting the Ramganga near Lohar Chaur.

(4) Upliftment of the Ranikhet Ki Dhar and Aira Deo (parts of the Lesser Himalayas) in the southeastern part of the basin, in Mid-Miocene times, led to the development of the Gagas River, a major tributary of the Ramganga.

(5) Formation of the Siwalik range in End-Miocene times not only changed the course of the Ranganga from southerly to southwesterly, making it a longitudinal consequent in the sag between the Lesser Himalayas and the Siwaliks, but also led to the development of gorges near Chaknakul and Tumeria, where the river cuts across the Kaligaon and Akiri Danda ranges of the Siwaliks. Its antecedent character is quite evident at both the places.

(6) Lateral corrasion and aggradation followed by successive upliftments and stream rejuvenation resulted in the development of flood plains and four prominent levels of terraces in the lower parts of the Ramganga and its major tributaries during Pleistocene and Recent times.

(7) Scree deposits, associated with fault-line and other scarps, as well as colluvial deposits are of recent origin.

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AN APPRAISAL OF RESOURCES FOR ECONOMIC DEVELOPMENT OF HAZARIBAGH PLATEAU : A GEOGRAPHICAL ANALYSIS.

Onkar Prasad Sup. : *Dr. R. N. Mathur*

The present study aims to analyse the existing resources and their potentials for the future socio economic development of the Hazaribagh Plateau : a part of the north-eastern resource region of India. A 'Community Development Block' or 'anchal' has been taken as the smallest areal unit for the present study, and a total of 90 maps and diagrams have been incorporated to clearly bring out the different spatial patterns of economic activity in the area.

The study has been divided into 9 chapters. Chapter 1 ('Introduction') deals with the meaning of resource, resource appraisal and economic development, the delimitation of the study area and its geology, relief, drainage and climatic characteristics. The area is mainly composed of two groups of rocks : (a) the Archaean System, and (b) the Gondwana System.

Physiographically, the area is divided into two units, each exhibiting a distinct erosional surface, that is : (i) the Upper Hazaribagh Plateau and (ii) the Lower Hazaribagh Plateau. The area comprises of six main drainage systems : the Damodar, the Sakari, the Mohane, the Amanat, the Lilajan and the Morhar.

Chapter 2 deals with a study of the natural resources, that is, soil water, forest and mineral. In general, the patches of lowland areas are comparatively more fertile. The red soil is extensively distributed, covering 62.34% of the study area.

Water supply is obtained both from surface and ground water sources. Area under irrigation accounts for only 9.14% of the net area sown, the share of subsurface and surface water being 5.60% and 3.54% respectively. The forests, accounting for 47.98% of the area, have been broadly grouped into : (a) the Tropical Moist Deciduous and (b) the Tropical Dry Deciduous. The total forest produce, comprises of timber and firewood, bamboo, tendu leaf, sabai grass, salai wood, sal and palas seeds, khair, mahua and lac, valued at about Rs. 28 million in 1976-77.

The study area forms the most important part of the 'Bihar Mica Belt' which contributes about 45% of the world's supply of high quality

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sheet-mica. The other minerals are : Copper ore, feldspar, beryl, quartz, fireclay, steatite, vermiculite and lead ore.

Chapter 3 deals with agriculture. The cultivated area percentage (36.1%) in the study area is far below the average for the state (63.3%). The main crops grown are paddy (45% of GAS), maize (10.14%), wheat (4.56%) and fruits and vegetables (6.19%). The average cropping intensity (111.8%) is rather low due to low level of development in technical skills and infrastructural facilities. The livestock density (146/km^2) is also low as compared to that of the state (161/km^2).

Chapter 4 presents a detailed account of population characteristics and human resources. The growth rate of population is high (+25.72% for 1961-71). The density of population (average : 179/km^2) varies from 62/km^2 to 640/km^2, mainly due to variation in topographical conditions. The urbanization in the study area as a whole is rather low (11.16%), it is very high in some pockets like that in the Bermo block (81.69%). The working population (average : 30%) is widely distributed, varying from 25% (Hazaribagh Block) to 36% (Bishungarh Block). Literacy (15.72%) is lower than the state (19.94%).

The population/resource regions of the study area, determined on the basis of selected variables, are designated as 'dynamic', 'transitional', 'prospective' and 'problem' regions. Further, the population potential regions have been delineated on the criteria of population and of distance amongst the urban centres of the study area.

Chapter 5 on 'Transportation' is devoted to a study of its evolution, network, road density, accessibility and traffic flow. The area records a road density of 12.1 km per 100 km^2 or 66.1 km per 100,00 persons, both of which are higher than the state average (7.5 km/1000 km^2 and 18.2 km per 100,000 persons).

Chapter 6 takes into account the distribution, reserves and production of coal, thermal and hydel power and the development of different industries in the area, in which the mineral and forest-based industries occupy a predominant position. The total estimated coal reserves (20,000 million tonnes) account for 58.4% of the state reserves. About 99% of the total production of electricity in the study area is coal-based. The main industries in the study area are in the form of coal washeries, coke oven plant and explosives factory all run on large-scale basis, apart from mica, glass, stonechips, furniture, biri, katha, silk, lac, country liquor, paper and pulp, oil pressing and oil-dal mills which are run on small or cottage level.

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Chapter 7 is devoted to a study of the 'stages and levels of resource development'. Relative indices, pertaining to agriculture, industry, transportation and literacy have been derived and areas of 'high', 'medium' and 'low' levels of resource development delineated therefrom.

Chapter 8 ('Planning for Development') deals with spatial variations in per capita income and service centres. For proper evaluation of resource-potential-trend, resource efficiency regions have been demarcated. Finally, planning regions of various orders identified, problems related to resource development in each studied, and proposals put forward for their future development. Chapter 9 : 'Summary and Conclusions', is followed by a bibliography of all the publications consulted or referred to in the work.

INTEGRATED RURAL AREA DEVELOPMENT PLANNING : A CASE STUDY OF MARIAHU TAHSIL, DISTRICT JAUNPUR

Chandra Bali Pal Sup. : *Dr. D. N. Singh*

The study area, Mariahu Tahsil (District Jaunpur), situated between 25°23′ N to 25°44′N latitude and 82°23′E to 82°45′15′′E longitude is one of the backward tahsil of Eastern Uttar Pradesh. It embraces 4 development blocks (Mariahu, Barsathi, Ram Nagar and Rampur) incorporating 724 villages grouped into 46 nyayapanchayats with an area of 827.5 km² and a total population of 506,551 (496,026 rural and 10,525 urban). Structurally, it is a part of the more or less a homogeneously plain alluvial tract of middle Ganga Valley. Having predominantly an agrarian society with heavy population pressure on land and less developed secondary and tertiary sector, it is characterised with agro-based and poorly developed economy.

Compressed into 7 chapters, the study starts with the *Conceptual Framework* wherein the concept of Integrated Rural Area Development planning and some of its associated aspects have precisely been discussed along with a note on objective and methodology of the study. To follow, in the 2 chapter : *Geographical Background* some salient physical features i.e. location, drainage, physiography, geology, climate, soil and natural vegetation etc. have been described to the extent they bearing on the development.

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Chapter 3 : *Physical Resource Base* has primarily been devoted to an appraisal of various aspects of land and water resources of the area. In this regard, a critical survey is made of general land-use (area not available for cultivation 7.95%, culturable waste land 11.65% and cultivated area 80.40%), double cropped area (52.56% of N.S.A.), cropping intensity (152.56%) and land-use efficiency. Land-use efficiency has been computed taking into account 5 variables i. e. land not available for cultivation, culturable waste land, cultivated land, irrigated area and area sown more than once. It is recorded as high (ranking co-efficient value below 5) in 3 nyayapanchayats and low (ranking co-efficient value above 20) in 13 nyayapanchayats Water resource has been studied with reference to irrigation (63.84%) and pisciculture. So far only 25 ponds have been brought under use for fisheries development.

Chapter 4 : *Human Resource and Settlements* encompasses a perusal of both the qualitative and quantitative aspects of population. As such, distributional pattern and density of population (general 612 persons/km^2, physiological 802 persons/km^2 and agricultural 205 persons/km^2) have been analysed along with an acconnt of different categories of working force (30.78%), literacy (25.58%) growth rate (28.71%) during 1971-81) and age-sex structure. The study of some relevant components of settlements is also included in this chapter.

In a bid to provide a comprehensive treatment to agriculture, almost the sole base of economy, some of its aspects, e.g. constraints of agriculture, cropping pattern and measurement of agricultural efficiency/ productivity have been detailed in ensuing chapter 5 : *Resource Utilization Pattern*. It is observed that agricultural productivity in most of the nyayapanchayats is low which can be ascribed to poor adoptation of modern farm-technology. Development of agriculture and allied activities and general industrial structure, which has not yet reached a considerable magnitude, have also been clubbed in this chapter. Proper organization of service centres is viewed as one of the essential ingradients of integrated rural area development planning and so, its various aspects viz., distribution of functions, functional hierarchy, identification of service centres, their hierarchy and complementary regions etc. have been described under the head *Spatio-Functional Organization* (chapter 6). There have been noticed 4 functional hierarchy groups, 39 service centres (1 of first order, 4 of second order, 12 of third order and 22 of fourth order).

The last chapter (7) *Planning for Integrated Rural Area Development* is a culmination of analysis made in preceding six chapters. There-

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in various proposals have been advanced for planning the socio-economic components in an integrated manner. Also, there have been suggested some readjustments in the existing administrative boundaries of the blocks from standpoint of effective and efficient administration. Need for the improvement in drainage system, flood control and soil conservation has been stressed in the context of physical problems.

Conclusively, it has been noted that agriculture being the mainstay of economy in the area needs a comprehensive planning, which does necessitate changes in general land use, crop orientation, increase in productivity with provision of assured irrigation, application of appropriate technology and modern inputs, viz., fertilizer, H.Y.V. seeds and crop protection measures. In this context, organization of agricultural produce with provision of requisite infrastructure, e. g., well linked market and credit facilities and conclusive pricing policy is deemed as inevitable. In addition, proper development of agriculture and allied activities and rural industrialization have been construed as viable strategies because of having inherent advantage of providing rapid economic growth vis-a-vis employment opportunities. Under agriculture and allied activities development there are included dairy, pisciculture, poultry farming, piggeries, sheep and goat rearing and horticulture. It is imperative to develop these activities particularly in view of no scope for further horizontal extension in agricultural land and, at the same time, demand for growth in vegetal cover.

While planning for rural industrialization, emphasis has been laid on utilizing, as far as possible available local resonrcrs. So there have been proposed agro-based small scale and cottage industries, such as flour and oil mills, rice mills, Khandsari, carpet and blanket making, bamboo-basket making, saw-mills, plastic works, cold storage, fruit processing, etc. It is anticipated that modernization of agriculture will also provide new opportunities for the development of industries like manufacturing and servicing of agro-implements, i.e. trolleys, ploughs, hoe and threshers, some spare parts and plant protection appliances etc.

In order to improve the quality of life, which is a major concern of present day planning, it is rather a must to provide socio-economic facilities/services within reach of entire population. Planning for such facilities has been extended on the basis of areal functional gaps and peoples demand. For this purpose, a well organized framework of service centres, taking into account spatio-functional as well as temporal aspects, has been suggested for 2001 A. D. There has been taken due

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care of efficiency of service centres which does require a comprehensive transport network commensurate with growing necessities in the changed context. In the last a model has been proposed emphasizing integration of all the three dimensions—spatial, functional and temporal of rural area development.

CLIMATIC CHARACTERISTICS AND WATER BALANCE OF BIHAR

Binaya Pandeya Sup. : *Dr. N. Prasad*

The study area Bihar (21°55′N to 27°31′N and 83°21′E to 88°17′E) is a unique state for the study of climate and water balance as it covers parts of the Himalayan foot-hills, the Ganga plain and the Chotanagpur plateau. The state spans over an area of 174038 km² lying on either side of the tropic of cancer and comprises 36 districts.

The study has been divided into six chapters. Chapter I deals with the physical personality of the area including the structure, land forms, drainage, soil and natural vegetation. Chapter II is devoted to climatic characteristics, which have been assessed on the basis of the spatio-temporal variations in climatic elements, i. e., temperature, rainfall, humidity, wind direction and velocity, number of rainy days and frequency of atmospheric disturbances (hail, fog, thunder and dust storms and squall). The climatic specialities of the state have thus been diagnosed. The spatial variations in the distribution of climatic elements over the state are influenced by a host of factors like degree of continentality, absolute relief, nature of the surface, presence of escarped plateau edges and vegetal cover. More than 80% of the annual rainfall occurs during the southwest monsoon period whereas about 5% is received during the winter season. The mean annual rainfall varies from over 1800 mm in the north eastern corner of the state to below 1200 mm in the central western part of the state along the Ganga axis.

The variability in rainfall varies from above 25% in the Purnea district to below 20% over the plateau. Ranchi plateau records more than 80 rainy days whereas in the western part of the plain it is 50 days only. The mean annual temperature throughout the state is above 23°C above and varies from 23.8°C at Ranchi to 27.0°C at Dehri-On-Son. The annual mean maximum temperature ranges from 29°C to

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34°C although the mean summer maximum touches 38°C and exceeds 46°C in May during the hot westerly wind 'Loo'. On the other hand, in the wake of cold waves, the lowest temperature touches 4°C. Heat waves and cold waves are generally experienced from April to June and from November to March respectively. The plateau region is free from heat waves. Temperature anomaly and diurnal and annual range of temperature are higher in the plain than over the plateau. Climographs and hyther graphs have been drawn to assess the importance of climate with respect to human comfort and suitability to crops.

In Chapter III climatic classification of the state has been worked out on the basis of Lang's Rain factor (1920), De-Mortonne's Aridity Index (1926), Koppen's scheme (1936), Kira's index of Moist and Dry climate (1945), Ayoda's adequacy index (1973) and Thornthwaite's scheme (1955). Among these the Thornthwaite's scheme has gained popularity mainly because PE and moisture index are considered in determining the climatic types.

Chapter IV deals with the spatio-temporal variation of climatic water balance components, i.e. PE, AE, soil moisture recharge, soil moisture utilization, water surplus and water deficit which have been computed on the basis of Thornthwaite's (1955) and Penman's (1963) methods for the 16 meteorological stations of Bihar based on the monthly normal data (average for 1931-60). The results on the basis of Thornthwaite have been compared with Penman's results. Yearwise water balance for an 18-year period (1951-68) of the 16 stations have also been computed in order to determine the trend of variations in water balance components. The average water balance components (1951-68) have been compared with those obtained from the normal data.

Chapter V is devoted to floods, droughts, and ground water conditions in the area. Aridity index, humidity index and moisture index of each station have been computed yearwise for the 18 year period (1951-68) and representative drought and rainy years have been recognized for each station. The severity of flood and drought have been analysed and flood and drought-prone areas have been delineated. Water surplus and water deficit in drought and rainy years have been compared with those of the normal year. Fluctuations in water table were studied with the help of data for 70 observation wells for the period 1972-80, and it has been observed that fluctuation is greater in the plain than in the plateau region.

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The present study has exposed a number of problems related to spatio-temporal variation in climatic elements and consequently in water balance components. Floods, droughts, inadequacy of seasonal rain for agriculture and extremes of temperature and humidity with respect to human comfort are some of the problems. Remedial measures for solving them to some extent, have been suggested as they directly affect the agricultural and industrial prosperity of the state. It is felt that the governmental machinery in the state should improve the condition of water mangement, which is today far from satisfactory.

INTEGRATED RURAL AREA DEVELOPMENT OF LAR BLOCK, DISTRICT DEORIA (UTTAR PRADESH) : A STUDY IN MICRO-LEVEL PLANNING

Arvind Kumar Singh Sup. : *Dr. N Prasad*

This work was undertaken for an intensive study of the Lar block for its integrated rural area development. This block is situated in southern part of Deoria district, eastern Uttar Pradesh. It extends from 26°-06′-45″ N to 26°-15′-30″ N latitude and 83°-53′-20″ E to 84°-02′-20″ E longitude with an area of about 177.37 Km^2 and a population of 1, 15, 220 persons as per 1981 census. It comprises of 145 settlements, out of which 25 are uninhabited and 120 are inhabited. There is only one urban centre at Lar.

Topographically, the area under study is almost a level plain. The Ghaghara flows along the southern boundary and its tributary, Chhoti Gandak, joins it on the south-east boundary of the study area. Both these rivers are notorious for bringing dangerous floods in the area and about 95 Km^2 are affected by floods every year.

Although the study area lies in the sub-tropical climatic belt, yet the monsoon, with all its rhythms, vagaries and extremes reigns supreme here. The occasional heat waves of summer are injurious to crops. In winter, occasional frost also does great injury to standing rabi crops. The study area has an annual rainfall of about 114 cm. Rabi crops, which are very important in the area, recieve only 2.14 per cent of the total annual fall. The rainfall variability has a great impact upon the cropping pattern and irrigation in the area. Under these climatic conditions, irrigation is essential for rabi crops and as a safety measure, during the spells of no rain, during kharif season. The study area has

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enough under-ground water resources, which can easily meet the irrigation demand. On an average, the soils of the study area are found to be medium in nitrogen, low in phosphate and medium in their potash content.

The study area is primarily an agricultural region, but it is unable to meet the food requirements of its own population. It was facing an annual deficit of cereals and pulses to the extent of about 1,500 and 2,560 tons respectively in 1981. No doubt, various efforts have been made to increase the agricultural production, but the same has been thwarted due to inadequate irrigation facilities, roastering of power, scarcity of fertilizers, poverty of farmers, restricting mechanization of agriculture and difficulties in securing cheap credit for these purposes. Thus, the agricultural sector has almost reached its saturation point under the present setup to sustain any additional population, which is increasing with a decenniel growth rate of 20.29 per eent.

The industrial backwardness of the region is apparent from the fact that only 5.21 per cent of the total working population is employed in this sector. The infrastructure facilities are also not adequately provided. The region is far behind in rural electrification. Only 34.00 per cent of the population is literate and the educational institutions are insufficient. The medical and public health services are not adequately provided. The extension services too, which create a progressive rural structure, are not adequate. So is the case with banking, credit co-operative and marketing facilities in the study area. The transportation facilities are poor. There are patches, which are beyond 3 Km of any type of road and are quite inaccessible. The village and feeder roads are very few. It is encouraging that the metre-guage railway, serving the area, is going to be converted into broad-guage.

Thus, it is evident that the area under study presents a picture of stagnant and decadent economy with increasing poverty and unemployment. The inducement of economic growth through 'Growth Centre Strategy' may be an ideal remedy for its integrated development.

Integrated area development can be defined as a comprehensive planning for the economic development of a specific geographical area. It involves the functional and spatial integration of settlements, which depends much on their centrality and hierarchy. The various methods for the measurement of centrality of functions and central places and their hierarchy have been tested by various authors with reference to various parts of India. In the present context, efforts have been made

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to test the feasibility of some of those methods and out of these, two methods are worth mentioning for the area under study.

In one of these, centrality of settlements is measured on the basis of five components, i. e., functional presence, functional dependency, functional inter-dependency, functional status and services potentiality of settlements. A five-tier hierarchy from V to I was obtained by this method and the number of settlements was found to be in order of 1:4:3:63:49 from V to I level respectively. The main drawback of this method is that the hierarchy of settlements is purely based on functional complexity and is not correlated with the population size and the population served, e. g., Padri Gajraj which serves an area of 1.81 Km^2 and a population of 555 is placed at the IV level, whereas Chanduki which is serving an area of 6.40 Km^2 and population of 3,965 is placed at the III level. Numerous such anomolies were noticed during this exercise and it was concluded that this method is not suitable for the purpose of this work where planning of growth centres for an itegrated area development is involved.

In the second method, the measure of centrality includes (i) population size of the settlements, (ii) degree of functional complexity of the settlement, and (iii) population served by the settlement. Firstly, the level of functional hierarchy were established on the basis of their medium population thresholds of 39 functions, which were considered for this exercise. A three tier functional hierarchy emerged. Functions of each level were awarded appropriate weightages and centrality scores of all settlements on the basis of functional complexity were ascertained. The 'space preference' of the people were analysed at all the above mentioned three functional levels, which depicted cluster of settlements dependent of specific centre at each level. This helped in identifying the central places and delineation of their service areas. The self-sufficient centres are the special features at first level. The space preference depicted the three-tier hierarchy of settlements and those at the III level were classified as 'development point', at II level as 'service centre' and those at I level as 'central village' for the purpose or this study. The rest of the settlements are either self-sufficient of dependent villages.

For centrality, the scores abtained by the centres on the three above mentioned criteria were combined to obtain a single integrated score. This exercise revealed that the 'development point', identified on the basis of space preferences for higher order functions also score very high (100) on the centrality score. The 'service centres' score lower (11-26) than the development point. The lowest order centres,

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i.e., 'central villages' and 'self-sufficient villages' score the minimum (11-01). Some of the self-sufficient villages, in spite of having quite high centrality index, are not central villages, because they are not serving any other settlement. However, these are the prospective central villages of the area. There is also a high correlation between the centrality and the population size and population served; the Spearman's correlation coefficients were found to be 0.69 and 0.95 respectively and are statistically significant at 0.01 level.

The space preferences also indicated some central places, which are located outside the study area, but have functional interaction with some settlements of the study area, e.g., two settlements of the study area dependent on Sohagra of Bihar for the functions of I level. Thus, this method was found suitable for the purpose of this study as it allows to measure the hierarchy of functions as well as settlements. The space preferences help in identifying central places and delineation of their service areas irrespective of their location inside or outside the study area. The area and population served by a central place become instrumental in finding the 'areal functional gaps' on which the planning for integrated area development depends.

It is evident from the foregoing discussions that the study area is being served by the central places of three successive level of functional hierarchy. It is also to be noted that higher order central places perform higher order functions alongwith the lower order functions. However, it is not necessary that higher order centres should perform all the lower order functions. Lar, which is the highest order central place in the study area, performs only 11 out of the 16 first level functions.

The hierarchy of centres that emerges from this study does not strictly conform to any of the three principles postulated by Christaller. The successive centres were found to be in the progression of 1 : 2 : 11 in the study area, which is nearer to the progression of K=3 hierarchy. Although the numerical progression shows much deviation from K=4 hierarchy, i.e., the transport principle, yet the distribution and location of centres show that this principle is operating ih the study area to some extent. The development point is located at major road link connecting the centres of the same and higher order located outside the study area. All the second level centres, i.e., the service centres are on major roads connecting neighbouring centres of the same level and atleast two successive higher order centres located inside or outside the study area. Most of the lowest order centres are also connected with service centres by good roads. Only the dependent villages have weak

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links with their central villages and hence, they are indiscriminately located. Thus, the spacing of the central places is more or less governed by the transport net and this is one of the reasons as to why there is no definite pattern in spacing of central villages and the dependent villages. It is also felt that easy accessibility affects the shape and size of the service areas. Elongation of service area of Pindi service centre in east-west direction along the road is an example.

The central places of second level have been found suitable for planning purposes, because the functions considered at this level are fairly central and there are many other settlements which have the capacity to sustain them. Planning at the first level will make the area a 'closed system' and space preference will be out of question at this level. Planning at the third level will only strengthen the single centre, i.e., Lar. The second level has, however, a link between the third and the first level. The study area is being served by 3 central places of second level, which have been classified as 'service centres.' As this level has been taken for planning, the study area has been divided into 3 planning sub-regions, i. e., Lar, Pindi and Bariha Hardo.

The analysis of the adequacy and inadequacy of the services in a sub-region indicated the areal functional gaps. The adequacy and inadequacy of a particular service depends on the 'standard' of the service in the regional context, which is related to the population and the area served by the service centre. The exercise for the functional standard by unit population revealed that Lar sub-region is deficient in communication, transport, extension services and village industries. Bariha Hardo shows deficiency in medical facility only, whereas, Pindi is deficient in all the functions. On the functional standard, by unit area basis, Lar sub-region shows deficiency in extension, Bariha Hardo sub-region in education, health and finances whereas, Pindi sub-region is deficient in all the services. These clearly indicate the functional gaps, and the deployment of functions/services in these gaps is essential for achieving a better functional integration in the study area.

On the critical examination of the functional gaps, 55 settlements have been proposed for deployment of various functions. The deployment of these functions at appropriate location will achieve a better standard in the sense that the gaps between the developed and underdeveloped parts will be reduced to the maximum possible extent. The deployment of new functions will also raise the status of certain centres. 4 such centres, namely, Mathiara Jagdish, Ajna, Sajaon and Bardiha have been identified as prospective 'central villages' and 2 centres, i.e.,

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Chanduki and Churia as prospective 'service centres' provided the functions as proposed for them are deployed there.

The spatial organisation of central places for 2001; A. D. has been planned. The number of central places have been suggested in the progression of 1:5:18 from III to I level respectively. By developing these second and first level centres, rural people can easily be served in respect of their specific needs, for which they will be dependent on 4 and 13 centres respectively. However, it has to be noted here that feasibility of planned spatial organisation depends on two factors. Firstly, the transport system as planned must be achieved and secondly, the various policy functions, as recommended, must be deployed at the planned central places by 2001 A. D.

The study reveals that the horizontal linkages between the same level centres are more or less absent due to lack of functional specialization, because all of them are performing the same functions at a certain level. Out of the three service centres of the study area, only Lar possesses the third level functions and all other service centres interact with Lar for the functions of this level. The whole region is under the influence of Gorakhpur, which is a much higher level centre and may be taken as 'growth pole.' All the service centres of the study area interact with Gorakhpur directly through rail or road.

The service centre of the highest order identified in this study is also the Block headquarter centre, but the service area delineated on the basis of space preferences of people does not tally with block boundary. Thus, it is obvious that to increase the efficiency, it is advisable that the block boundary should be the same as delineated by the space preferences and hence, it is recommended that 2 settlements of Salempur block and 7 settlements of Bhagalpur block should be transferred to Lar block so that a settlement should remain under the influence of the same service centre and the same block. This will improve the shape of the block with 0.81 shape index, which may be considered as approximately ideal.

The success of above growth centre approach of integrated area development depends much on ideal network of roads. The study indicates that the links between the service centres, development point, tahsil and district headquarters are well established. The links between the centres are found to be weak in certain cases and the links between the central villages and their dependent settlements are very weak in most of the cases. Thus, it is proposed that all the dependent villages be connected with their central villages by katcha roads. The links, which

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are weak or absent between the central villages and their respective service centres, as indicated, must be completed by constructing about 31 Km of pitched or non-pitched metalled roads. The metre-guage railway line, serving the area, should be converted into broad-guage as early as possible.

The projected population figures, at an interval of 5 years on the basis of 1981 population, reveal that the population till 2001 may increase by about 45 per cent over the 1981 figure. By that time, the area under study will have to cater to the needs of additional 52,100 persons. The projected food requirements reveal that at the present rate of agricultural production, the area will be facing a deficit of 9,260 tons of cereals and 4,110 tons of pulses by the year 2001. Not only this, even the labour force in 2001 may rise to 57.651 persons or 17.951 persons more than what it was in 1981 and the provision of employment to these people is one of the major problem considering the fact that even the present labour force is not fully employed. Thus, any planning of agricultural and industrial sectors has invariably to take into consideration these burning problems of the study area.

A critical review of agricultural efficiency in the study area reveals that all the sub-regions have moderately developed cultivation but at the same time, they have to cope with high population pressure. It is also concluded that the area has more or less exhausted its soil resources and has become almost stagnant. However, the gap between the carrying capacity of land and the population pressure on it may be minimised to maximum possible extent by adopting the following measures :

(1) If proper efforts are made, atleast about 1,108 hectares of additional land may be brought under cultivation, raising the net sown area from 12,088 to 13,196 hectares.

(2) It is visualised that the double cropped area may be increased from 3,944 to 10,566 hectares, thus, raising the gross cropped area to 23,752 hectares.

(3) It is essential, for achieving the above, to raise the irrigational potential to about 19,199 hectares by 2001 A. D., and this may be done by installing tube-wells/pumping sets as indicated in the study.

(4) The new crop rotations, as suggested in the study, should be adopted to raise the agricultural efficiency to some extent and to avoid the practice of keeping the land fallow.

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(5) In view of the above changes, an alternative cropping pattern has been suggested and it is recommended that the same should be achieved gradually and finally by 2001 A. D. This planned cropping pattern aims at an increase of about 12.45 per cent area under cereals, 358.14 per cent under pulses and about 219.67 per cent under commercial crops over 1980-81. Although the share of food crops in the overall pattern has been reduced from 96.19 to 91.79 per cent, the share of paddy, wheat, maize, gram, peas and arhar has been increased in view of the objective of food self-sufficiency and future calory requirements of 2001 A. D.

(6) It is essential to achieve the objectives of agricultural sector by assuring the supply of future fertilizer requirements as projected in the study. The appropriate location of centres have already been suggested in connection with spatial and functional organisation planning for the effective distribution of fertilizers and other agricultural overheads and implements.

(7) Social forestry can play a very big part in improving the economy of the farmer. In the area under study, about 2,735 hectares of land may be available for social forestry, which will solve to some extent the problems of firewood, fixture, furniture and agricultural implements, edible fruits, industrial raw materials and unemployment. In addition, this will help in improving the ecological imbalance.

(8) Dairy farming, on small scale, should be introduced in the study area to provide subsidiary occupation to agriculturists and to supplement their income. After overcoming the hurdles pertaining to dairy farming, as indicated in the study in detail, it will be advisable to establish two milk collecting centres, one each at Bariha Hardo and Pindi.

(9) The main hurdles in the mechanization of agriculture in the study area are finances and repair facilities. It is suggested that hiring centres of agricultural implements should be established at each 'service centre.' It is also recommended that either government should establish 'maintenance cells' or private intrepreneures should be attracted by providing maximum subsidies to establish such workshops at all 'service centres', i. e., at Lar, Pindi, Bariha Hardo, Churia and Chanduki to look after the repair works of agricultural implements on appropriate charges. Co-operative societies should arrange for providing financial loans.

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(10) These planned agricultural developments can not be achieved without agricultural credit and crop insurance. 11 additional co-operative societies have been planned and their proper locations have also been recommended. It is also essential for the government to introduce and popularise the crop insurance scheme in the study area.

If the aforesaid are implemented, it is envisaged that the study area will gradually make up its present deficiency of foodgrains and will have almost 2,440 tons of surplus foodgrains by the year 2001 A.D. Indirectly, with the increase in farm output, the study area will not only achieve self-sufficiency in foodgrains, but at the same time, agricultural processing and servicing industries will expand considerably all over the area.

The resources of the study area are confined to a few agricultural and livestock products. However, it has cheap labour and vast market and hence, some of the resource-based and demand-based industries have good scope in the region. The development of agricultural sector, as planned in the study, will contribute a great deal by providing agro-based raw materials and creating demand of agricultural implements and their repair facilities. On these assumptions, a broad assessment of the industrial possibilities was made and a number of medium and small scale industries and their appropriate locations have been recommended. In the present situation of the study area, the development of medium and small scale industries by itself should be regarded as a growth factor to break the vicious circle of inactivity, stagnation and poverty.

For the industrialization of the area, it is quite necessary to establish a few large scale industries as these will create scope for the establishment of anciliary units also. Thus, it is concluded that manufacturing units producing plastic goods, electronic parts and equipments and cycle tyres and tubes may be established at Lar. A number of oil mills can also be established.

The field survey revealed that certain types of rural industries like atta chakkies, rice haulers, oil ghannies, earthen pot making, amber charkha, carpentry / blacksmithy, etc. have a good scope in various suh-regions. Recommendations have been made to establish these in selected 'central villages'.

The growth centre approach in industrial planning leads to conclude that a 'central village' should have rural industries, 'service

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centre' medium and small scale industries and 'development point' should have large scale industries for proper integration. Keeping this in view, the location of the proposed industries have been suggested.

It is expected that the discussion, projections and recommendations contained in this study will be instrumental in achieving a better integration of settlements and functional system, which is basically needed at present and this will ultimately lead the area towards a high level socio-economic development.

TRANSFORMATION OF THE RURAL HABITAT IN DHANAPUR DEVELOPMENT BLOCK (DISTRICT VARANASI)

Harishchandra Singh Sup. : *Dr. Onkar Singh*

The thesis consists of seven chapters. First chapter is devoted to introduction in which the concept of rural habitat transformation and the general outline of the area have been discussed. The process of transformation in its real sense involves change in totality. The rural habitat simply signifies the rural environment or the rural landscape. In a country like India wholesale change in rural landscape, i.e., 'transformation of the rural habitat' may hardly materialise. However, transformation of the rural habitat is a process to solve the problems for the effective involvement of the local human and physical resources to improve the socio-economic and ecological conditions of the rural areas. The Development Block of Dhanapur forms the study area which extends from 25°26′58″ N to 25°34′20′′ N of latitudes and from 83°15′44″ E to 83°32′13″ E of longitudes. It is located in the north eastern part of Chandauli tahsil in Varanasi district, U. P. and covers an area of 231.75 sq kms. The block comprises 138 villages grouped into thirteen nyayapanchayats. The area is mainly drained by the river Ganga which makes it northern and north-eastern boundary. The sandy, sandy loam, *karail* and clayey are the main soil types.

The second chapter deals with agricultural aspects of the rural habitat transformation. The consolidation operation of land holdings began in the area in 1970 and by the time of field work for the present thesis 127 villages were covered. A sample study of two villages reveals that after the consolidation the number of field plots has decreased and the average size of the plots has increased resultantly. In 1980 the area not available for cultivation, cultivable waste and cultivated land shared 13.98, 8.62 and 77.40 per cent of the total area respectively. In most of the villages the increase in the cultivated land during the last

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two decades has been less than 15 per cent. The irrigated area has increased from 34.20 per cent of the total cultivated land in 1961 to 56.72 per cent in 1980. It shows a fast intensification of the cultivation. Presently more than half of the cultivated land gives at least two harvests. The paddy and wheat are the main crops of the area.

The third chapter of the present thesis deals with agricultural innovations in the area. Out of the total 138 villages (including sixteen uninhabited ones) one hundred and eleven are found to have the mechanical innovations. Only 825 families (out of more than 18000 families) are found in possession of one or more types of agricultural mechanisation. The tractor, electrified tube-well and diesel oil operated water pumping set were introduced in the area in years 1940, 1968 and 1960 respectively. The three above noted innovations at work in the study area in May 1981 were counted as 93, 472 and 312 in that order distribute over 51, 75 and 84 villages respectively. The numerical growth of the power operated paddy husker, thresher, chaff-cutter, sugarcane crusher and tractor trolley has strongly followed the increase in number of power affording innovations, i.e., the electrified tubewell, diesel pump set and tractor. The introducing years for pesticide sprayer and bio-gas plant are 1970 and 1967. These innovations were confined only to 38 and 26 villages with 51 and 37 pieces respectively in May 1981. To compute different level mechanisation indices 'Scoring' and 'Indexing' techniques have been devised. The growth and other aspects of the agricultural mechanisation has been discussed with reference to certain most relevant correlates. The consolidation operation has boosted up the growth of agricultural mechanisation.

The details of the population have been discussed in the fourth chapter. The population in the area (1, 25, 404 persons in 1981) is almost evenly distributed with an average density of 5 persons per hectare in 1981. Following increase in the population size the number of villages sharply decrease. A big increase in the total population during the last three decades is noted. The projected population of the area for 2001 A. D. comes to about 0.20 million (2 lakh). The 1981 census puts the literacy rate at 32 per cent. The proportion of females in the literates is fast moving up.

The fifth chapter of the thesis is devoted to the character and transformation trends in settlements and the social system. Generally the compact and hamleted settlements are found in the area. These are dominated by the Gaharwar Rajputs who first came to the area in the 14th century and gradually established the present network of settlement. In recent years some farmers have been establishing farm houses in their chaks. Presently twenty two service centres are identified amongst which

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two are first order, four second order and sixteen third order centres as per hierarchical categorisation. Pertaining to the *jajmani* system, religious and social trips, untouchability, etc., have been discussed.

The public utility services and non-agricultural activities make the theme of sixth chapter. The development of the utility services has generally come up during the post-Independence period and the growth of the non-agricultural activities is still a later development which is running only in its initial stage. The area is presently possessed with only road transport, Dhanapur being the main transport hub. In May, 1981, the settlements housing the Primary Schools, Junior High Schools, High Schools, Intermediate and Degree Colleges were counted as 57, 19, 9, 6 and 1 respectively in the area. The area has got one Primary Health Centre (PHC), four public dispensaries and four veterinary dispensaries. Presently twenty post offices are available in the area. Three commercial banks are also functioning there-two at Dhanapur and one at Kamalpur. In recent years the non-agricultural activities have got impetus due to the subsidies and support offered by the government as also because of the heavy pressure on farming and preference for white-collared jobs by the educated youngers.

The last chapter of the thesis is devoted to transformation planning and suggestions for streamlining and enhancement of the ongoing development. To meet the increased food requirements the agricultural production also needs to be increased. The installation of a number of government owned tubewells is highly called for to increase the double cropped area particularly that belonging to the small farmers. To maintain the ecological balance, check the soil erosion and to raise fruits, flowers, fuel wood, etc., on local scale social forestry is recomended. The landless labourers need be provided special financial assistance under a clean administrative machinery to buy cows, buffaloes, sheep, goats, etc. The poultry farming is also to be encouraged. The existing network of service centres is proposed to be turned into a network of four first order, eight second order and twentyfour third order centres. For effective flow of services from the centres planned for the purpose of construction of certain metalled roads and two bridges is planned. A few privately run educational institutions should be regularized and one High School and two girls' Intermediate Colleges are to be newly established. To render adequate medical facilities to the people some other service centres should also be equiped with public dispensaries. To check the population boom and to improve the quality of life in general strict adherence to family planning should be observed. The electricity must be provided to all the villages in the area as early as possible.

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GEOLOGY

HYDROCHEMICAL STUDIES IN BHADOHI BLOCK, GYANPUR TAHASIL (VARANASI DISTRICT) AND EFFECTS OF LOCAL POLLUTION

Zohair Hazzaa Sup. : *Dr. S. G. Karkare*

The present work embodies the hydrochemical studies of a part of Indo-Ganga basin in the flood plains adjacent to Bhadohi covering the entire Bhadohi Block of Gyanpur tahsil, Varanasi district of Uttar Pradesh. The salient features of the work are as follows :

1. Field work and sampling

For collection of water samples from state tubewells and dugwells in Bhadohi Block; sampling of the surface waters and Varuna river, Morwa river and Khorowa and Newada tals, three field session were utilised to achieve this work and more than 300 samples were collected in batches designated I, II and III. Of these, batches designated I and III were collected during March 1982 and March, 1983 while batch II was collected in September, 1982 immediately after heavy rains during monsoons.

Samples were also collected for pumping test from three tubewells (Nos. 83, 85 and 195).

Six water samples from different locations were collected for bacteriological analysis. Soil and mud samples from Varuna and Morwa rivers were collected along with samples of soil and overburden in five boreholes (Tubewells) at regular intervals upto 100 m depth. Two samples of wartc water effluents from Woollen factory (Carpet Industry) were also collected.

A record of other data like well location, depth of sample, size of casing, water temperature, odour, colour, turbidity etc. is made with each sample.

2. Analytical Data and Analytical Techniques

(*a*) *Water analyses*

All water samples were analysed for their pH, specific conductivity (in the field with a portable pH conductivity meter that records

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temperatnre also) and T.D.S., CO_3, HCO_3, NO_2, NO_3, SO_4, PO_4, Na, K, Ca, Mg, Cl, SiO_2, N, F, B, Zn, Mn and Cu. All analyses were reported in standard formats employed at the Water Research Laboratory, Varanasi.

In samples analysed for pumping test for pipe corrosion / reaction etc. following determinations were made pH, specific conductivity, T.D.S., Na, K, Ca, Zn, Cu, Mn and Fe.

(*b*) *Soil Analyses*

Fortyfive (45) soil/overburden and channel mud samples were analysed for organic carbon, pH, electrical conductivity, T.D.S., available PO_4, available potash, Na, K, Ca, Cu, Mn, Fe and Zn. They were also tested for traces (ppb level) of Cr by neutron activation technique.

Analytical methods and instrumental techniques employed for this work include :

(a) Field measurements—water testing kit, pH papers and portable pH conductivity meter.

(b) Laboratory determination—Standard titrimetric, colourimetric and turbidimetric procedures were employed for several determinations. Besides, these, rapid methods of spectrophotometric and atomic absorption spectrophotometric analyses were also employed. Neutron activation method was utilised for traces of Cr in soil samples.

(c) TEM and SEM techniques besides X-ray diffraction (powder method) were employed to confirm the clay mineralogy.

3. Data presentation

All data mustered by the author have been presented in standard formats. SEM, TEM and X-ray diffraction pictures have been included as plates besides photographs of equipment used. Relevant standard and calibration curves are also annexed. Computations and transformation of data have been explained wherever necessary for specific graphic illustrations etc. All relevant information is well tabulated in the text or appended to the work.

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4. Chemical characteristics of water and quality of water etc.

All the waters have been characterised compositionally and classified with regard to their suitabilty for specific exploitation such as potability, irrigation, industrial use etc. Relevant inferences have been drawn in regard to possible hazards. Pollutions have been identified as :

(a) Biological and (b) Chemical—dissolved species.

5. Anomalous concentration and sources of pollution :

In regard to dugwells (shallow aquifer) it has been pointed out that they show anomalously high concentration of several dissolved chemical species and the causes of such pollution and pollutants have been discussed at length. Following conclusions have been drawn in regard to the pollution in the shallow aquifer :

(*i*) *In regard to their suitability for drinking purposes*

(a) According to the W.H.O. drinking water standards (1971, 72), the quality of water from most dugwells is unsatisfactory due to very high MPN. The quality of waters from several dugwells suffers from high TDS and several others have objectional levels of fluoride.

(b) Waters of all tubewells are suitable for drinking.

(*ii*) *Suitability for Irrigation*

One dugwell DW 58 is unsatisfactory (very high TDS, high sodium etc.). Others range from moderate (Class C_3 S_1) to good (class C_2 S_1). Four wells (including DW 58) were found unsuitable because of high permeability index (High Na and bicarbonate). On the basis of potential salinity index (PS) the same four wells including DW 58, DW 79, DW 81 and DW 199 are found unsatisfactory. There is a distinct case for magnesium hazard (from dugwell waters) to crops. This is further aggravated by high sodium content of waters. Water level fluctuation—the level being close to ground—and evapotranspiration and capillary action all render the soil more saline in this case.

(*iii*) *Suitability for industrial purposes*

The waters high in TDS are not suitable for boiler feeds. Dugwell waters mostly belong to this category. Tubewell waters except TW No. 302 are useful for washing and cleansing linen. Dugwell waters are not suited for silk and dye industry nor for tannery.

6. Recommendations have been made for overcoming diffuse pollution and site specific point pollution.

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SAND MATA PARAGNEISS COMPLEX : ITS STRUCTURAL AND PETROLOGIC ANALYSIS (DISTRICT UDAIPUR, RAJASTHAN)

Mallickarjun Joshi Sup. : *Dr. R. S. Sharma*

The so-called Sand Mata Paragneiss Complex (Topo Sheet Nos. 45 G/14 and 45 K/2; lying between north latitude 25°30′ and 25°35′ and east longitude 73°57′ and 74°01′45′′) of Gupta (1934) forms a part of the Archaean basement complex (3.5 to 2.6 b. y.) in Udaipnr district of Rajasthan State in northwest India. The rocks (area 53 sq km) consist predominantly of basic garnet granulites in which inclusions of aluminous paragneisses and subordinate garnet-diopside amphibolite are found. This rock complex at Sand Mata is surrounded by schists and augen gneisses, also belonging to the basement complex which Heron (1917) called Banded Gneissic Complex and regarded it as the oldest stratigraphic unit in NW Indian Shield. The contact between the granulites and the surrounding schist-gneiss association is marked by a shear zone. Mafic dykes, mostly norite in composition, intruded the 'inner' rock complex and have been partially recrystallized during granulite facies metamorphism which affected the basic granulites and their included amphibolites and metapelites.

In the basic granulites the mineral assemblages are characterized by the development of garnet-clinopyroxene-quartz in a reaction rim or corona around orthopyroxene against its contact with plagioclase suggesting the reaction :

$$opx + plag = gt + cpx + qz$$

which in complex system is divariant and occurs with increasing pressure at the boundary of the intermediate (or medium) pressure to high pressure granulite facies of Green and Ringwood (1967). Hornblende occurs, in addition to clinopyroxene or replacing it, in the corona at the orthopyroxene/plagioclase boundaries. Some hornblende may also be primary.

The limiting assemblages in the Al-rich metapelitic inclusions are kyanite-garnet-biotite-quartz-plagioclase-sillimanite ± K-feldspar and kyanite-cordierite-garnet-biotite-quartz-plagioclase±K-feldspar in which kyanite is overprinted by sillimanite and later followed by the development of second generation kyanite occurring mostly as needles. Common pelitic compositions contain hypersthene-biotite-quartz-K-feldspar-garnet ± plagioclase which is a charnockitic assemblage in a sense.

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The petrologic evidence in the "inner" rock complex is consistent with the earlier observations of Sharma and Narayan (1975) that the Banded Gneissic Complex rocks are polymetamorphic. In the first metamorphic event (M_1 2580 Ma) the assemblage orthopyroxene- plagioclase was stable in the basic composition while the pelitic inclusions contained the stable kyanite-garnet-biotite-quartz-plag (with muscovite) association. During the second metamorphism (M_2 = Delhi cycle, 1600-950 Ma) in which higher pressures were developed, the orthopyroxene-plagioclase became unstable and developed the garnet-clinopyroxene-quartz corona around orthopyroxene in the basic granulites. Sillimanite and kyanite(2) as well as cordierite developed in the aluminons paragneiss inclusions. The petrographic observations do not preclude the possibility that orthopyroxene was once in contact with Al_2SiO_5 in an earlier stage of M_2 event, although orthopyroxene and sillimanite/kyanite have been observed only in one thin section of the metapelite.

Structural studies showed that three phases of deformation have affected the Sand Mata Complex, similar to that found in neighbouring area of the Banded Gneissic Complex. The F_1 are isoclinal reclined folds with W to SW orientation of their fold axes. These were superposed by F_2 folds with their fold axes trending in NNE-SSW to NE-SW directions. The F_2 folds in the basic granulites reveal a Vortex or "Schlingen" structure with vertical to very steep plunges. F_3 folds are only broady warps in the area. The pegmatite-aplite veins developed during the high-grade metamorphism or emplaced as melts from deeper levels have a distinct time relationship with the phases of deformation, as revealed from the orientation of these quartzofeldspathic veins in relation to fold styles in the rocks.

Static conditions of granulite metamorphism is documented in the preservation of garnet-clinopyroxene-quartz corona around orthopyroxene which probably quenched at deeper levels before emplaced into shallower levels. The preservation of this high pressure (and high temperature) assemblage of garnet-clinopyroxene-quartz in the basic granulites is attributed to decreasing reaction rates at low temperatures and to lack of penetrative deformation. Recrystallization of granulite conditions is also noticed in norite dykes in which garnet developed near the orthopyroxene-plagioclase boundaries, and hornblende formed around the pyroxenes. The norite displays clear igneous (ophitic) texture in most samples.

The surrounding schists and gneisses contain biotite, quartz, plagioclase, K-feldspar and garnet in various combinations The presence of muscovite in these rocks is secondary in origin.

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Composition of the minerals, mostly rim compositions, have been determined for the assemblages of basic granulites, aluminous metapelites, norite and amphibolites. The plotting of compositions of adjacent minerals on suitable phase diagrams and the distribution of elements, particularly Fe, Mg and Ca in coexisting mineral pairs showed equilibrium conditions amongst the assemblages that were found texturally stable in basic granulites and their included rocks at Sand Mata.

The Fe-Mg exchange in the mineral pairs garnet-biotite and garnet-cordierite in metapelites and orthopyroxene-clinopyroxene, garnet-clinopyroxene and garnet-orthopyroxene in basic granulites of Sand Mata have been used for temperature estimates by applying different geothermometric models. At the same time solid-solid reactions and silicate-based barometers (cordierite-garnet, garnet-plagioclase-kyanite-quartz, garnet-orthopyroxene-plagioclase-quartz, garnet-clinopyroxene-plagioclase-quartz) have been used for pressure calibrations.

Determined P-T conditions during granulite metamorphism based on thermodynamic calibrations in the basic granulites indicate a wide range of temperatures from about 900°C to 650°C with concentrations at 850°C and 650°C; while in the pelitic inclusions calculated temperatures are in the vicinity of 600°C. There is, however, no evidence that the basic granulites had higher temperatures than the metapelitic inclusions, since relict phases (sillimanite, mesoperthite, hypersthene, etc.) indicating high temperatures are also found in the metapelites. The wide range of temperatures in the basic granulites is considered to reflect temperature range from that of the initial formation down to final equilibration. The absence of high temperature in the metapelites in the same range obtained in the basic granulites, and the variations in different mineralogical thermometers in the basic granulites, are attributed to the kinetics of readjusting reactions (during re-equilibration) which must not agree for different exchange reactions.

Geobarometry of the basic granulite and metapelitic assemblages gave comparable pressures from 10 kb to 5 kb, well within the kyanite stability field. These pressure estimates for basic granulites are, however, not all consistent with the high pressure granulite field to which the Sand Mata granulites belong in view of the unstability of orthopyroxene-plagioclase pair (Green & Ringwood, 1967). Moreover, the pressure values in metapelitic assemblages are 3 kb higher than obtained for basic granulite assemblages. The pressure variation in the basic granulites is found to show a correlation with X_{Ca} in garnet. It is conceived

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therefore that the proposed activity model for garnet may not hold good for these grossular-rich garnets of Sand Mata granulites. It is suggested that different P values in the basic granulites reflect control of bulk composition and/or activity in garnet and plagioclase. The pressure values, however, show concentrations at about 9 kb and 5 kb at the same temperature of 650°C. From this it is inferred that the Sand Mata rocks recrystallized at deeper level (35-40 km depth) were subsequently uplifted to shallower depths where final quenching occurred. This conclusion is also consistent with the geological setting of rocks as well as with their textural and mineralogical criteria.

The difference in P-T results between pelitic inclusions and their enclosing basic granulites may be taken to indicate that the elemental ratios of minerals did not completely re-equilibrate to the conditions at which they were emplaced. It is difficult to determine where in the metamorphic evolution the present element ratios finally occurred. But it seems almost certain that Sand Mata Complex after reaching its maximum depth conditions corresponding to about 10-12 kb experienced a dramatic period of rapid uplift which probably ceased in the vicinity of 5 kb. From this point it shared the further metamorphic history with the surrounding unit. The garnet-clinopyroxene-quartz corona around orthopyroxene against plagioclase in the basic granulite has been ascertained to have been produced during prograde metamorphism at temperatures of about 850°C and pressures near 8 kb. This conforms to several observations besides the temperature-pressure estimates from (garnet-clinopyroxene-quartz) corona assemblage. These are : (i) the restriction of the corona forming reaction opx + plag = gt + cpx + qz to orthopyroxene/plagioclase; (ii) fairly consistent widths of the corona layers; (iii) water deficient environment otherwise orthopyroxene would be metastable; (iv) occurrence of hornblende replacing clinopyroxene or in addition to it in the corona and (v) very gentle dP/dT slope of the reaction and therefore the temperature independency of the corona forming reaction.

Water pressure during granulite metamorphism was less than load pressure is indicated by the general lack of evidence of partial melting and the absence of muscovite in the metapelitic inclusions together with the presence of P_{H_2O} P_{total} indicating assemblages such as cordierite-kyanite-K-feldspar, and cordierite-garnet-Al_2SiO_5-quartz-plagioclase-K-feldspar (Hensen & Green, 1973; Schreyer, 1968; Holdaway & Lee, 1977) in the metapelites. The activity of water has been calculated from thermodynamic modelling of the reaction bio + ky + qz = gt + Ksp + H_2O so nicely documented in the metapelitic inclusions. The calculation gave very low a_{H_2O}, in the range of 0.15 to 0.26. The hypothesis of CO_2

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influx from mantle in the vapour phase to form charnockitic assemblages is ruled out in view of the nature of occurrence of hypersthene-bearing metapelitic rocks, which are included within basic garnet-granulite.

The reason for higher pressure recorded in the pelitic inclusions than in the enclosing basic granulite is difficult to interpret but for want of an alternative it is attributed to differential expansion mechanism of the pelitic inclusions and host granulite.

The P-T estimates combined with (i) textural relations of basic granulites, (ii) the kyanite-sillimanite as well as hypersthene-biotite-garnet-quartz-K-feldspar relationship, (iii) the ubiquit ous occurrence of kyanite needles with random orientation, and (iv) the core-to-rim calibrations of pressure, have been considered to be sufficient grounds for deducing P-T paths during metamorphic evolution of the Sand Mata Complex. From about 850°C and 8 kb conditions the Sand Mata granulites under went nearly isobaric cooling during which intrusion of norite also occurred. The textural and P-T criteria in the norite mineralogy support its intrusion during waning stages of granulite metamorphism. The conversion of hypersthene into biotite and hornblende occurred in this cooling path, and some of the "back relations" such as

$$\text{hyp} + \text{Ksp} + H_2O = \text{bio} + \text{qz};$$
$$\text{cd} = \text{gt} + \text{ky} + \text{qz}$$

and the growth of kyanite (needles) after sillimanite are the outcome of this cooling history of the rocks.

Further cooling continued until the rocks attained about 600°C within the kyanite field where higher pressures of 10-12 kb (recorded from garnet rim-plagioclase-kyanite quartz barometer of Newton and Haselton (1981) were generated, probably due to underplating of basic magmas in this part of the crust. This was followed by uplift to the surface due to tectonic phenomenon, perhaps as an isostatic response to density contrasts with the country rocks.

These exhumation P-T paths contrast strongly with the isobaric cooling paths which are characteristic of terranes where metamorphism is related to igneous intrusions (Phillips and Wall, 1981). They also do not resemble the cooling paths predicted for crustal thickening by structural duplications or tectonic thickening modelled by instantaneous overthrusting where temperature increases by conductive relaxation whilst concurrently pressure decreases by erosion of the tectonically thickened pile (England and Richardson, 1977; Wells, 1979). The type of P-T paths identified in this work from samples of Sand Mata granu-

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lites cannot also be characteristic what some metamorphic terranes seem to have developed in a facing plate margin at a subducting plate boundary, e.g. the Khtada Lake metamorphic complex in the coast Mountains of British Columbia (Hollister, 1979).

The deduced P-T paths for Sand Mata complex are compatible with the England and Richardson (1977) model for crustal thickening by magma addition. Our P-T estimates lead to the conclusion that during the granulite metamorphism the average geothermal gradient was about 30°C/km and the temperature higher than 850°C. The higher pressure estimates of 10-12 kb at about 600°C corresponds to a depth of about 40 kilometers if an average density of 2.85 gm/cm^3 is assumed for the overlying rock column. Thus the Sand Mata granulites are clearly of deep crustal origin and presumably represent part of the pre-Aravalli continental crust on which Precambrian supracrustals (Aravallis, Raialo and Delhis, collectively 10000 m thick) were deposited with an angular unconformity. The age of this crust is not known but recent radiometric dating on Banded Gneissic Complex and its equivalent rocks from nearby areas give 3.5 b. y.; the main phase of granulite metamorphism is indicated in the time span 1600-950 Ma (called the Delhi/Aravalli orogenic cycle by Sharma, 1977, 1983). Geochemical characteristics for major oxides on the basic granulites and comparison with terranes suggest oceanic tholeiite as the parent rock for the basic granulites at Sand Mata.

PRIOSTRATIGRAPHICAL AND PALAEOECOLOGICAL STUDIES OF THE BATHONIAN—CALLOVIAN ROCKS IN KHAVDA—SADHARA AREA, PACHCHHAM 'ISLAND' (KACHHA, GUJRAT)

Dhirendra Kumar Pandey Sup. : *Dr. S. K. Agrawal*

The classic region of Kachchh on the western coastal margin of Indian shield represents shelf part of Indus-Baluchistan geosyncline. It is renowned for the thick pile of Jurassic sediments and their prolific endemic fossil faunas. The oldest exposed strata, lying directly but unconformably over an igneous complex resembling Mundwara Complex in Rajasthan (Jaitly, Karkare, and Singh, 1980), are now dated Upper Bajocian (Jaitly, 1981). The Lower Callovian beds present an amazing example of expanded succession. Thus, Kachchh Jura enjoys a unique position in world stratigraphy.

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The strata are disposed in the form of three parallel, east-west trending, faulted anticlinal ranges and an isolated mass of Wagad. In all they constitute six "uplifts" or "highland areas", *viz.* Kachchh Mainland, Wagad and "Island Belt" comprising Pachchham, Khadir, Bela and Chorad "Islands". These are separated from each other by "residual depressions" (Rann and Banni). "Premordial fault pattern" in the pre-Cambrian basement seems to have controlled the tectonics (Biswas).

The "Island Belt" constitutes the northern anticlinal range of Kachchh Jura, and Pachchham "Island" is its westernmost component. In the southern part of this "island" is Gora Dongar ("White Hill") which encompasses the map-area between Khavda town (23°50'33" N : 69°43°49" E) and the village of Sadhara (23°44'38" N : 69°54'40" E). It is roughly 100 sq km in extent and falls within topo-sheets Nos. 41E/9, 13 & 14 on 1:50,000 scale. The area represents a hilly range with a series of crests not exceeding 200 metres. The relief is concordant.

Existing literature largely deals with the Mainland. Save the stratigraphic column of Goradongar Formation recently described briefly by Biswas, there is no detailed published account of the Jurassic rocks of the area. Initially the present work was started under the supervision of Dr. C.S.P. Singh (since deceased) and has now been completed under the guidance of Professor Dr. S. K. Agrawal. It forms a part of a comprehensive plan to describe the fossils collected bed by bed, to establish precise stratigraphy and to interpret depositional environment of Kachchh Jurassics, which was initiated by late Professor Dr. Rajnath and is still in progress in the Department of Geology, Banaras Hindu University.

The present author has geologically mapped the area for the first time on 1 : 15000 scale. The vertical column (approx. 175 m + thick) comprising 30 beds has been established. Out of the huge collection, 1402 fossils (1225 bivalves and 177 cephalopods) collected bed by bed have been described. Biozonation with the help of local fauna has been attempted. Palaeoecological conditions have been inferred on the basis of fossils and sediments.

A good part of the present succession is common with Jaitly's Kala Dongar sequence (northern part of Pachchham "Island") because of repetition/omission of certain beds due to a longitudidal fault just to the north of the area. Hence, a *composite column* (about 575 m + thick) for this "Island" as a whole has been compiled (jointly with Dr. Jaitly) under a new formation, *Khavda Formation*, named after

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the *taluk* Khavda, instead using two formations separately, *viz.* Kaladongar and Goradongar Formations proposed by Biswas, for the two hill ranges of respective names.

The above-mentioned new formation has been subdivided into five informal members : Chapparbet member (75 m), Pachhmaipir member (320 m), Kharidongari member (10 m), Taga member (135 m) and Kakkar member (35.5 m+) in ascending order. The oldest member is absent in the present area. Bed Nos. 1-13, 14-16, 17-19, and 20-30 belong to the four younger members respectively. Their lithology varies widely both vertically and laterally. Broadly, in the present area, the Pachhmaipir member consists mainly of sandstones, the two succeeding members are essentially calcareous and the youngest member is dominantly argillaceous. The limestone of Kharidongari member is at places "golden oolitic".

The strata are disposed in a series of anticline and synclines. Besides the major fault referred to before the area is affected by several minor faults. Numerous igneous intrusions in the form of sill and dykes invade the sedimentary strata.

The bivalves are distributed in eight orders, namely, Nuculoida, Arcoida, Mytiloida, Pterioida, Trigonioida, Veneroida, Myoida and Pholadomyoida, represented by 27 families consisting of 49 genera (and 13 subgenera) and 115 species. Two genera—*Kachchhinucula* and *Agrawalimya*—and one subgenus, *Indomya*, have been newly created; three genera/subgenus, *viz. Linetia* ? Chavan, (*Antiquicyprina*) Cassey, *Orthonota* ? Conrad have been recorded here for the first time from India.

Among the species the following 21 are new to science :

Nuculana (*Praesaccella*) *pachchhamensis*, *Indoculana sadharaensis*, *Grammatodon* (*Indogrammatodon*) *agrawali*, *Lycettia kanjilali*, *Modiolus* (*Modiolus*) *singhi*, *Isognomon* (*Mytiloperna*) *saxenai*, *Camptonectes* (*Indonectes*) *ramalraoensis*, *Ctenostreon rajnathi*, *Plagiostoma sornayi*, *P. andhouensis*, *Rastellum* (*Arctostrea*) *pandeyi*, *Trigonia* (*Trigonia*) *bipartita*, *T.* (*Latitrigonia*) *bhattii*, *Vaugonia* (*Orthotrigonia*) *parwatiae*, *Protocardia* (*Protocardia*) *arunaae*, *Ceratomyopsis bilobata*, *Pholadomya* (*Pholadomya*) *goradongarensis*, *Pholadomya* (*Pholadomya*) *abhayi*, *P.* (*Indomya*) *kachchhensis*, *Homomya giganteous*, *Agrawalimya pseudosulcata*.

Six species, *viz. Meleagrinella ovalis* (Phillips), *Camptonectes* (*Camptonectes*) *rigidus* (J. Sow.), *Plagiostoma notata* (Goldfuss)

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Neocrassina (*Neocrassina*) *elegans* (J. Sow.), *Nicaniella* (*Nicaniella*) *bulla* (Roemer), *Ceratomya concentriea* (J. de C. Sow.), have been recorded for the first time from India/Kachchh. As many as 64 forms are an addition to the specific list of Khavda-Sadhara area. Among the known forms, several have been considered conspecific because/ of intergrading specimens while the characters of some have been emended and still in a few cases generic assignment has been changed. In a number of cases the vertical ranges have been extended, mostly downward. *Plagiostoma notata* Goldfuss and *Nicaniella* (*Nicaniella*) *bulla* (Roemer) occur in Kachchh at horizons different from those at which they are found in Europe. *Meleagrinella echinata* (Smith) is not confined to Callovian, contrary to the supposition of Kanjilal and Singh (1980).

The cephalopods comprise 56 species assigned to 19 genera (and 5 subgenera) belonging to five superfamilies, namely, Nautilaceae, Phylloceratacea, Spiroceratacea, Stephanoceratacea and Perisphinctaceae, constituting two orders—Nautilida and Ammonoidea. Interesting to add that about 70 per cent of the total cephalopods studied belong to the family Macrocephalitidae.

Among cephalopod genera/subgenera, *Clydoniceras* Blake, *Micromphalites* Buckman, (*Clydomohalites*) Arkell, *Bullatimprphites* Buckman, *Gracilisphinctes* Buckman have been reported for the first time from Indian Jurassics. Save *Bullatimorphites*, all of them are typical Bathonian ammonoids. Further, seven species have been given new names and three have been described for the first time from Kachchh, even India (listed below). In addition, 11 species, although known from Kachchh Mainland, were not yet reported from Rann Islands and 34 are an addition to the specific list of the present area. (New species)—*Phyloceras giganteus*, *Clydoniceras pachchhamensis*, *Clydoniceras triangularis*, *Macrocephalites* (*Macrocephalites*) *inflata*, *Macrocephalites* (*Macrocephlites*) *amrawatiae*, *Macrocephalites* (*Dolikephalites*) *jaitlyi*, *Gracilisphinctes indianā*.

(First record from Kachchh/India)—*Bullatimorphites bullatus* (d'Orbigny), *Gracilisphinctes progracilis* (Cox and Arkell) and *Gracilisphinctes arkelli* Collignon.

On the whole it has been seen that the old divisions of Kachchh Jura put forth by Waagen, and modified by Rajnath, are basically lithostratigraphic (but for terminology) mappable units, very well developed in Kachchh Mainland, and are finely applicable at least to this region. For the Rann Islands, on the other hand, different formation names

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have been introduced by workers. This is, in fact, necessary till the various sections have been measured and described properly along with faunal details. In so far it concerns the biozones established by Spath they have been used here in local stratigraphic sense only.

Khavda-Sadhara beds range from Bathonian to Callovian. Definite Bathonian and undisputed Oxfordian rocks are not hitherto known from Mainland and Rann 'islands' respectively; Callovian zones, however, are well developed in Mainland. Accordingly, the correlation of the beds of the author's succession has been done with those of Rann "Islands" and that of Callovian strata with the exposures in the Mainland as well. For this both megafossils (bivalves and ammonites) and lithology have been taken into account. The inadequacy of faunistic details or/and paucity of ammonites has/have permitted only broad correlation. However, some of the beds in the upper part of the succession could be dated precisely because of certain characteristic ammonites.

Among the constituent beds of Pachhmaipir member, the Bed No. 1 corresponds Jaitly's Bed No. 14 of Kala Dongar* to an extent in lithology. Bed No. 9 is characterized by *grandidieri-baroni-lyrate* assemblage besides the occurrence of many other bivalves. In view of fossil content and lithology this bed has been equated with Western Bela* Bed No. 17 and Umrapur* Bed No. 4. Kala Dongar Bed No. 21 is shelly sandstone. In between, the present Bed No. 6 has been correlated with Jaitly's Bed No. 19 and Western Bela Bed No. 15 whereas lithology of Bed No. 4 corresponds to that of Umrapur Bed No. 1. The member on the whole is of Bathonian age with the possibility of Upper Bajocian in its lower part; precise delineation is not possible and hence referred to as ? Lower-Middle Bathonian.

Next above, the Kharidongari member corresponds Bed No. 1 of Biswas.** Both fossils and lithology of Bed Nos. 14 and 16 suggest their correlation conveniently with Jaitly's Bed Nos. 28, and 30 & 31. In view of the findings of characteristic genera such as *Clydoniceras*, *Gracilisphinctes*, *Bullatimorphites* and especially the subgenus *Clydomphalites*, the member may be assigned Middle Bathonian age unhesitatingly and not Callovian to which Biswas has referred his Bed No. 1

* Details of Kala Dongar are given in Jaitly (1981); Western Bela "Island" in Rai (1972) and Singh and Rai (1980); Mouwana Dome in Agrawal and Kacker (1980); and Umrapur in Agrawal and Tripathi (1980).

** Reference of Biswas means his paper of 1980.

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(Flagstone member). Besides, (i) *Bullatimorphites bullatus* (d 'Orbigny), ordinarily taken to be a typical Upper Bathonian species, represent Middle Bathonian in Kachchh, and (ii) the "golden oolite" within this member does not correspond with any of its horizon encountered elsewhere in Kachchh.

The Bed Nos. 17 and 18 of Taga member are correlatable with Kala Dongar Bed Nos. 32 and 33 and Biswas's Bed No 2 (Gadaputa Sandstone member). The present Bed No. 19 is a marker-bed in view of its lithology, morphologic expression, i.e. marginal cliffs, and the appearance of *Macrocephalites*. It, therefore, corresponds Western Bela Bed No. 20, Mouwana Bed No. 14 and Umrapur Bed No. 9, at least partly. Jaitly's Bed No. 34 has identical lithology although it did not yield any fossil. All these beds (including present Bed No. 19) have been dated Lower Callovian whereas the author's Bed Nos. 17 and 18 being without ammonites and below *Macrocephalites*—yielding bed have been dated Upper Bathonian.

Lastly, the Bed Nos. 20-29 of Kakkar member represent probably partly the Modar Hill member (only Bed Nos. 4-6) of Biswas. *Macrocephalites* spp. have been recorded from Bed Nos. 20 and 26-29. Therefore, these Beds (Nos. 20-29) together with immediately older Bed No. 19 (Taga member) constitute *Macrocephalites* Range zone. They can be correlated with Jumara* Bed Nos. 10-26, Jhura* Bed Nos. 16-18, Habo Hill* Bed Nos. 12-15 (Dhrang member) and Keera* Bed Nos. 1-5.

In the youngest unit, Bed No. 30, there is commingling of ammonite species assigned to different horizons by Spath. Evidence is more in favour of its reference to "Reineckeia Beds" and hence, Middle Callovian age.

Palaeoecological inferences have been drawn on the basis of macro-invertebrate fossils and nature of the sediments. On the whole the sedimentary sequence of the Khavda-Sadhara area was deposited in a basin with rapidly fluctuating conditions. There were abrupt changes vertically and sometimes laterally. The basin was very shallow and never attained a depth greater than the top of neritic zone. Faunistically, bivalves were far more abundant than other groups throughout the column but they, too, were irregularly distributed. Cephalopods made their appearance in upper half of the sequence and were sparse. Other biotic communities such as pygmy gastropods, corals and echi-

* Reference be made to Spath (1933, p. 740), Agrawal (1956, p. 162 and 1958, p. 125), Kanjilal (1974, chart 1) and Mitra *et al*. 1979, p. 140) respectively.

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noids became important at times. Among bivalves infaunal elements dominated over the epifaunals. Moreover, brackish water forms were more in number than in kind whereas reverse was true for marine ones.

PETROFACIES AND PETROLOGIC EVOLUTION OF PRECAMBRIAN BANDED IRON FORMATION AND SILICICLASTIC ROCKS NEAR KEONJHARGARH, KEONJHAR DISTRICT, ORISSA

Nagendra Pandey Sup. : *Dr. B. K. Chatterjee*

The present investigation concerns with the sedimentological attributes and depositional environments of the Precambrian Banded Iron Formation and siliciclastic rocks of the Kolhan Group exposed in and around Keonjhargarh (21°39′57″, 85°36′0″), Orissa. The Banded Iron Formation of Gandhamardan hill, which forms an outlier of Noamundi-Malangtoli-Khandadhar-Gua-Iron-Ore Belt, belongs to Noamundi Group and is restricted largely to the oxide facies of Lake Superior type. The sulphide and carbonate facies are commonly represented in sub-ordinate amount by pyritic black chert and tuffaceous shale formations. It is almost unmetamorphosed and exhibits many depositional and penecontemporaneously deformed sedimentary structures. Mineralogical composition is represented by about 95 percent hematite, martite, magnetite, chert, siderite (as pseudomorphs) together with very minor amount of goethite-limonite, stilpnomelane, chlorite, greenalite and pyrite.

The sulphide facies, which forms the base of the continuous sequence of BIF, comprises from bottom to top of intraformational black chert breccia, pyritic black chert and banded hematite-magnetite black chert. Except monotonous parallel laminations, no other sedimentary structure is visible in this rock. It indicates chemical precipitation under anaerobic, relatively quiet, below wave-base off-shore basinal condition. The basin was restricted or sealed from open sea towards west, so that pH and redox potential of water was mainly controlled by local geologic factors such as free circulation of sea water, neighbouring volcanism etc. The oxide facies consists of banded hematite jasper (jaspilite) and interbedded jasper and white chert or granule bearing siliceous formation (taconite). The presence of siliceous spherulite, stromatolitic structures, mudcracks, cross-aminations, ripple

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and rill marks, indicate the deposition of chemically precipitated iron and silica gel above wave base near-shore environment. The occurrence of intraformational brecciation, convolute laminations, pods, granules and other penecontemporaneous deformation structures at periodic intervals in the succession, suggest occasional water turbulence and current action produced due to sudden slumping or volcanic eruptive forces near the depositional site. The absence or paucity of detritals further indicate low relief of the surrounding continental areas and starved basinal condition.

The BIF of Gandhamardan hill has been devided into four distinct petrofacies types namely, iron oxide band (I), silica or jasper band (J), composite band (C) and penecontemporaneously deformed composite band (P_c), on the basis of colour, mineralogical composition, thickness, mode of occurrence of individual bands and sedimentary structural features. The application of first order Markov chain analysis reveals the following probable upward facies transitions or cycles significant above 99.9 percent level for 8 degrees of freedom.

$$(I)\rightleftharpoons(J)\rightleftharpoons(C)\rightleftharpoons(P_c)$$

Mutual substitutability analysis further reveals strong substitutability pairs between $(I)\leftrightarrow(C)$ and $(J)\leftrightarrow(P_c)$. At the lower horizons, BIF is characterized by low entropy-set values and slight asymmetric A-4 type of cyclic pattern whereas values for entropy-sets increase and gradually pass from B to C or mixed type cycle at topographically high areas. It reflects either the modification of individual band, especially composite band (C) by supergene processe or intermittent instability and change in water mass composition of the depositional basin.

Scanning electron microscopic (SEM) examination of BIF, especially of the jasper band (J), reveals two dominant type of surface textures—spongy and granular-crystalline, with all gradations between the two. The presence of numerous leached out microcavities and growth of platy hematite further indicate the role of supergene processes. The filamentous, coccoid and rod-shaped alga-like forms have also been encountered during the SEM investigations.

The sulphide and oxide facies are separated by thick purple silicified tuffaceous shale and interbedded variegated cherts. The tuffaceous shale is somewhat similar to altered pyroclastics described by La Berge (1966) from the BIF of western Australia. The sharp contact with overlying banded hematite jasper and underlying rock

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indicates that the deposition of BIF and volcanism commenced simultaneously with the initiation of geosynclinal development of the Noamundi basin i. e. with the development of off-shore structural buckles that subsequently formed island arcs characterized by volcanism. Mossbauer spectra of iron oxide band (I) indicate dominance of crystalline hematite (α—Fe_2O_3) and presence of Fe^{2+} in traces. Rare earth element (REE) analysis of the BIF reveals Eu^{2+} enriched and Eu^{2+} depleted patterns for the lower and upper horizons respectively which in turn reflect an increase in the oxygen content of the depositional environment. The general steep LREE enriched—HREE depleted pattern, further suggests the contribution of OMG gneiss, Dhanjori lava and pyroclastics in supplying the source materials. The abundance of magnetite in lower horizons (particularly black chert) as compared to upper horizons also indicates oxidation of Fe^{2+} to Fe^{3+} directly in sea water which caused vertical zoning of redox potential in the depositional environment. Iron band is believed to have been formed as a result of oxidation of upwelled water whereas prolonged evaporation caused precipitation of silica from the surface water. The BIF of Gandhamardan hill initially deposited in major parts as hematite – chert rock in a partially enclosed yoked or marginal basin. The occurrence of few skeletal crystals of magnetite and martitized magnetite grains in cryptocrystalline silica bands indicate their cogenetic relationships with the silica and hence possibility of derivation of hematite by oxydation of magnetite and remobality of iron oxide during diagenesis in subordinate amount, can not be ignored.

The Kolhan Group lies unconformably over the Noamundi Group, Singhbhum Cranite and OMG and consists of impersistent conglomeratic sandstone and medium to fine grained, moderately well sorted sandstone. These siliciclastic rocks are tectonically undisturbed and show low dip near the Singhbhum granite which progressively increases towards the west. In general the siliciclastic rocks show differential thickening and thinning phenomenon due to original basinal configuration tectonically controlled by NNE-SSW alignment of Noamundi basin or Singhbhum synclinorium parallel to the Eastern Ghat strike. An extensive recrystallization together with brecciation of siliciclastic rocks near BIF may be indicative of approximately N-S faulted contact. Five petrofacies have been recognized on the basis of grain-size, sedimentary structures and bed geometry. They are granular sandstone (P_1), sheet standstone (P_2), laminated sandstone (P_3), rippled sandstone (P_4) and thinly laminated siltstone sandstone (P_5). First order Markov chain analyses for the six measured vertical profile sections reveal the following preferred upward transition paths.

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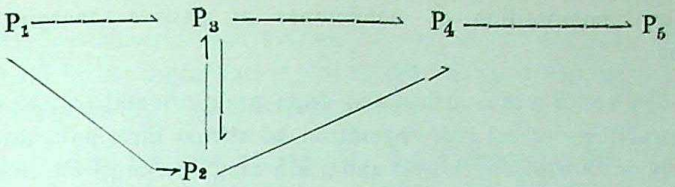

However, the value of chi-square in majority of the sections suggests that the geological processes ultimately operative in the deposition of the siliciclastic rocks were non-Markovian in nature. The occassional scouring or erosional surfaces with granule layers in P_2 & P_3, diffused nature of contact between P_4 & P_5, hummocky cross-bedding, reactivation surfaces and sharp ridges or steps over granule surfaces in SEM photographs, indicate the probability of storm event in nearshore environment. Extensive reworking of sands during deposition is further evidenced by the results obtained from sediment trend matrix analysis. The petrofacies and apparent vertical thickness distribution together with regional and stratigraphic variations of grain-size parameters indicate a slight depression in the west central and a general paleoslope towards western and southern parts of the basin. The stratigraphic distribution of size parameters reflects varying environmental energy condition such as water depth, wave intensity or velocity of depositing currents. The bivariant statistical and textural parameters, shape of the cumulative curves, linear discriminant function analysis and packing parameters, all indicate interaction of fluvial and nearshore environments. The C-M diagram of P_1 & P_2 reflects its similarity with the basic pattern of alluvial fan deposits while others indicate deposition in beach or nearshore environment approximately 10 to 40 meters depth. The substitutability analysis reveals a strong P_1 and P_3 mutual substitutability pair, while entropy suggests dominance of asymmetric A-4 or C type cyclic patterns. The plot of E (system) versus number of states further suggests neritic environment of deposition.

The Kolhan siliciclastic rocks are quartz arenite, quartzose arenite or wacke and lithic arenite types. They are dominantly mature to supermature quartz arenite consisting of about 90 percent non-undulatory, undulatory and polycrystalline quartz and subordinate amount of feldspars, muscovite and rock fragments. The rock fragments identified in granular sandstone (petrofacies P_1) are chert, red jasper, black chert, metaquartzite, banded hematite jasper, granite, opaque rounded hematite grains, basic lava and fuchsite-quartz-schist. The result of major element analysis of the siliciclastic rocks resemble closely to average

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chemical composition of sandstones of passive margin tectonic setting.

The vector means calculated from grain orientation and sedimentary structures reveal the operation of atleast three paleoflow system namely north-west, south-west and north-east, in almost all petrofacies. The relative vector strengths, however, vary laterally and vertically in these petrofacies, reflecting variation in flow regimes during deposition. In P_1 and P_3 the paleocurrents are mostly in NW and SW directions with dispersion lesser than 4000 and run parallel to lenticular or wedge-shaped sand bodies. This indicates fluvial influence during their deposition. Others, on the otherhand, exhibit NE, NW and SW components with dispersion more than 6000, reflecting on-shore (NE) directed storm induced marine currents and waves. The heterogeneity of clasts composition together with paleocurrent directions, suggest polygenetic nature of provenance rocks. This is also corroborated by the plot of quartz types in the diamond diagram after Basu *et. al.* (1975).

The Kolhan conglomerates and sandstones were deposited in high energy environment of a coastal complex near the margin of the Late Precambrian epeiric sea. The vertical and lateral arrangement of different petrofacies with their characteristic coarsening-fining upward sequences suggest the superimposition of retrograding shore-line features on earlier prograding humid alluvial fans-sandflat complex. Initially the petrofacies P_1 was formed as proximal alluvial fans near the granitic source terrain. This was reworked extensively by long-shore and off-shore currents, forming P_3 and P_2 as sandflats or beach whereas P_4 & P_5 formed barrier beach ridges or coastal dune system. Later on, due to high energy storm surge ebb currents, the entire shore-line complex was extensively reworked, giving rise the present configuration of petrofacies types of the Kolhan siliciclastic rocks.

GEOCHEMICAL STUDIES OF MIGMATITE COMPLEX IN THE VICINITY OF KERLAPAL, BASTAR DISTRICT (M. P.) AND THEIR BEARING ON Sn-Ta MINERALIZATION

Shiva Kumar Sup. : *Dr. S. G. Karkare*

The present work deals with the geology and geochemistry of granitoids in the vicinity of Kerlapal in Bastar district of Madhya Pradesh.

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After presenting a brief resume of the earlier works, the author has summed up his arguments regarding the choice of the area and the aim and scope of the present enquiry, viz.

(a) To map the area geologically for a thorough knowledge of field structural aspects of granitoids, their relation to regional lithostratigraphy and their detailed petrography.

(b) To sample and analyse the granitoids for their petrochemical characteristics, specialization and trends etc. The work also includes informative chapters and sections dealing with methods of analysis, instrumentation techniques etc. as well as an idea about the precision and accuracy of results that determine their reproducibility. It also includes date on a number of trace elements of interest, obtained by XRF techniques.

(c) To present all the field, petrographic and analytical data and transformations therefrom, to bring out effectively all petrochemical characteristics and trends suggested by the raw data. Relevant chapters and sections cover this aspect and diagrams, graphs, photographic plates (including field, specimen and thin section photographs) serve to illustrate the author's point of view.

The relevant summary of results are given at appropriate places in relevant chapters.

Finally all the results are thoroughly discussed providing alternative explanation of facts and/or phenomena.

the summarized account of important findings include the follwing :

(1) The area in the vicinity of Kerlapal is dominated by granitoids which more commonly include granite (granite gneiss) forming domical outcrops and occasional torr like hill masses-foliation being marked in the gneiss. There are only a limited number of hills represented by quartzite and diopside gneiss. It may be noted that there is no outcrop of granodiorite as reported Srivastava (1981).

(2) These rocks show transitional relation with the schlieric and nebulitic migmatites as well as with the enclosed patches of layered migmatites. Aplitic intrusions are minor.

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(3) Distict 'Zones of Migmatization' have been observed all along Malenger, Muler Vagu and Sabari rivers. The intensity of this process has led to a ratio of 1:15 or even 1 : 20 between the country rocks (now as enclaves) and the granitoid.

A complete sequence of migmatization and homogenization has been observed. The migmatitic complex exhibits all the major migmatitic structures and the structural sequence of mobilization in Malenger Valley is as follows :

Layered→Phlebitic→Folded→Wavy→Ophthalmitic→Schlieric→Schollon→Nebulitic

With the schlieric-nebulitic types dominating.

Migmatization is largely pre-to-syn tectonic and at least two episodes of migmatization can be inferred from the nature of rafts (folded stromatites) in metatexitic complex.

(4) Feldspathization, particularly, microclinization has been observed in the country rocks. This indicates a prior role of Na-K metasomatium episodes before migmatization stemming from anatectic mobilization. This conforms with observations of Hame (1965) and the complete sequence is as follows :

Regional isochemical metamorphism→Granitization with Na-K dominant metasomatism→Anatexis→Metatexis (Migmatization in situ)→Migmatization (Diatexitic)

and a corresponding observed transition—

Country rock→Migmatite→Gramite/granite gneiss.

(5) The observed data suggests that we have either

(a) *Granite as the and product of the process as outlined above.*

Or

(b) *A Granite Magma intruding the countr y rock producing hybrids and assimilating it.*

The observed facts, therefore, seem to substantiate Harmes (1959) plan to start with a granite melt—juvenile or palingenetic—and produce the observed metasomatic effects, in the context of Na-K metasomatites. The role of gas fluxing along deep fault planes (mantle degassing) has also been suggested as an alternative explanation for the process, as well as an Archaean heat source with geothermal gradient of 50°C/Km or more. With gradient values exceeding 50°C/Km or more the required P T conditions of Sillimanite Zone to which these granitoids belong are attainable at relatively shallow depths (<12Km).

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Metatexis as well as deep crustal anatexis are also attainable at levels of ≈ 12 Km (10-20 Km, according to Daly, 1933).

The present findings are in agreement with those of Srivastava (*op. cit.*) that the metasedimentaries (including the granitoids) reveal two episodes of metamorphism which are, viz.

(a) An earlier regional metamorphic event of high amphibolite facies Sillimanite Zone conditions (M_1) followed by,

(b) M_2 — a contact metamorphic episode at the acme of M_1 when granitic pluton is emplaced.

(6) Trace element data suggest an origin for granitoids as resulting from crystal liquid fractionation process i.e. either anatectic palingenetic or magmatic. The role of metasomatic activity has already been given earlier and its prior to the complex formation.

(7) Retrogressive changes include :

(a) Sericitization—of feldspar, garnet, kyanite, sillimanite and cordierite.

(b) Chloritization—pinitization of ferromagnesian minerals hornblende, biotite etc.

(c) Greisenization in the country rocks in the vicinity of granite with minor Sn-Nb-Ta mineralization.

(d) CO_2 Metasomatism—Talc formation (TT lenses)

(e) Uralitization of diopside.

(f) Micropegmatization and aplite formation.

(g) Epidotization in granite gneiss.

(h) Formation of Cataclasites from all rocks.

(8) Geochemical characterization of the granitoids suggests their being particularly low in their contents of MnO, FeO, MgO, total iron and poorer in CaO and TiO_2. They are richer in SiO_2 and K_2O.

(9) The geochemical characteristics are indicative of Sn-Ta-Nb mineralization. However, greisens are invariably poorly mineralized and the tenors and ratios of certain trace elements, particularly K/Rb clearly suggest the barron nature of the granitoids.

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GEOPHYSICS

STUDIES ON BROAD—BAND SYNKLYSMOTRON LENSES FOR SCANNING ELECTRON MICROSCOPE

Krishna Mohan Srivastava Sup. : *Dr. C. L. Singh*

Scanning Electron Microscopes are now coming into increasingly wide use as an important high resolution tool in almost all branches of science, technology, medicine and also in the industry, for the topographical studies of very small objects, particularly objects whose thin foils can not be made and are having rough surfaces. Thus, any improvement in the present state-of-art of these instruments will definitely lead towards the betterment of the researches in all the above fields.

With the advent of field-emission guns scanning electron microscopes with resolution of 30° A have become commercially available. However, in order to improve the resolving power of these instruments further, it is essential to correct their spherical aberration (C_s) as it is this aberration which ultimately sets the limit to their resolving power.

Vaidya (1972) developed a special type of high frequency lens system, which he termed as 'Synklysmotron Lenses'*, and experimentally demonstrated at the Cavendish Laboratory that these have the potentiality to correct the C_s by 70% at 15 KV and theoretically Garg (1977) has shown that it is capable of correcting C_s to the extent of 91% at 15 KV. Further, Pandey (1978) has shown that this lens system can as well be used as C_s-corrector even upto 10 MV.

Synklysmotron lenses consist of two identical re-entrant cavities, working as the bunching and the correcting lenses, separated by a field free drift space. One of the critical requirements for the optimum performance and maximum C_s-correction by these lenses, is that the

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* In Synklysmotron Lenses, the word 'Synklysmos' is a Greek noun which means 'an act of washing together (on a beach)' and 'tron' is the familiar ending for electron. The title Synklysmotron, therefore, stands for a process of washing the electron waves by means of electromagnetic waves, so as to clean them of aberrations. Since this principle has very significant applications in electron optics, the Synklysmotron system is classed as a lens.

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electrons must see a phase change of 120° of the r. f. field while traversing through an optimally fixed value of the cavity gap of these lenses. As the beam accelerating voltage is changed, due to the variation in the beam velocity, the transit time of the electrons through the cavity gap and hence the transit angle will change. In order to preserve the transit angle of 120°, the frequency of these lenses must be varied which is not possible as these lenses employ essentially the re-entrant cavity structures which are very sensitive to change of frequency. Thus the critical requirement of preservation of phase will entail different synklysmotron lenses for varying beam accelerating voltages. This is not a practical proposition as in the conventional scanning electron microscopes, the beam accelerating voltage is varied from 1 KV to 30 KV depending upon the need of the user.

Looking towards the immense potentialities existing in the synklysmotron lenses, this work has been taken up and persued further to overcome the above limitations and to find out some alternative systems which would basically give the same electron-optical properties as is obtained in the Synklysomtron lenses and simultaneously it should be a broad-band structure so that for all values of the aecelerating potential, the same single system should be capable of correcting the C_s inspite of different frequency requirement of the r. f. signal. As the variations in the frequencies are found to be lesser for the accelerating voltages upto 30 KV (which is the operational range of conventional scanning electron microscope) it has been the endeavour to design the synklysmotron lenses with broad band characteristics suitable for scanning electron microscopes.

Since the synklysmotron lenses operate in microwave region, the search was made for any available microwave structure which could provide wide-band characteristic. A comparative study of these structures and their limitations for use in synklysmotron lenses is discussed. As none of these structures, as such, were found suitable, a novel concentrically coupled cavity structure is proposed for use in synklysmotron ienses. The synklysmotron lenses incorporating these structures as their bunching and correcting lenses are named as BOARD-BAND SYNKLYSMOTRON LENSES

The organisation of the text is primarily in terms of the design of broad band synklysmotron lenses with respect to their expected band width and corresponding range of operational voltage.

The concentrically coupled cavity structure of the broad band synklysmotron lenses consists of a reentrant cavity whose outer wall

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forms the inner wall of a coaxial cavity and coupling slot is made in the common wall. The design details of the re-entrant and the dominant TM_{010} mode coaxial cavity are presented. A quantitative estimate of the variation in the values of the relevant operational parameters of the broad band synklysmotron lenses for use in scanning electron microscope was also carried out and the results are presented.

The analysis of this structure with a view to evaluate the maximum band width and the conditions there of, is possible by using its equivalent lumped circuit analysis due to the complicated boundary conditions. A simple computation scheme was developed for the evaluation of the band width for different values of cavity resonance frequency (f_c), slot resonance frequency (f_s), coupling coefficient K and an intrinsic parameter a_k. The values of f_c and f_s have been varied from 7 GHz to 10 GHz, and K and a_k from 0.1 to 0.9.

The results show that such type of coupling produces two pass-bands. The upper pass-band is always forward whereas the extent of the useful region in the lower pass band is limited by the term 'partial resonance frequency' (f_k). Lower band is also forward for $f_s < f_k < f_c$ whereas for other conditions it is backward (i. e. the group velocity is in the opposite direction to the phase velocity). This backward motion will cause suprious oscillations in broad band synkly-smotron lenses and therefore this region of the negative lower pass band is undesirable even when these lenses were operated in the upper pass band, which will be forward. Following these conditions, it has been possible to obtain the maximum useful band width of the upper pass-band only upto 42% corresponding to the values $f_c = 8$ GHz, $f_s = 7$ GHz, $f_k = 7.16$ GHz, $k = 0.2$ and $a_k = 0.9$. The extent of this much band width corresponds to the beam accelerating voltage from 10 KV to 24 KV only of the scanning electron microscope.

Based on the above analysis, the proposed concentrically coupled cavity structure was fabricated. A versatile electron-optical bench has also been constructed for the performance evaluation of the broad band synklysmotron lenses, but due to the practical difficulties the in-situ experimentation for the complete characterization of the broad band synklysmotron lenses could not be possible.

It has been concluded that the concentrically coupled cavity structures, designed with the above specifications, could be effectively used as the bunching lens and the correcting lens of the broad-band synklysmotron lenses. The broad-band synklysmotron lenses thus

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designed would be capable of correcting the spherical aberration (C_s) of the scanning electron microscope for its operational range of 10 KV to 24 KV.

It is hoped that these broad-band synklysmotron lenses when incorporated in scanning electron microscopes will successfully improve their resolving power to better than $10A^o$ and thus improve the present state-of-art in electron microscopy.

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MATHEMATICS

SOME POLYNOMIAL SETS OF TWO AND SEVERAL VARIABLES (SPECIAL FUNCTION OF COMPLEX ANALYSIS)

Alpana Bhatnagar Sup. : *Dr. B. D. Agrawal*

The present thesis entitled, "Some polynomial sets of two and several variables (special functions of complex analysis)" comprises five chapters.

The first chapter comprises a brief historical account of recent developments in the theory of hypergeometric functions of two and more variables and generalizations of classical as well as non-classical polynomials, given by different authors at different times. Most of these generalizations and unifications are particular cases of the unified polynomial sets defined by us in chapters II to V. I have arranged different unifications and generalizations given by different researchers chronologically. For greater detail, one may refer to the list of references given at the end. Next in §1.9, we have given some notations, which we have used, time and again, in our work of the present thesis. I have concluded this chapter by giving a set of two lemmas of a general character; which have been used extensively off and on.

In Chapter II, an attempt has been made to define a polynomial set of two variables (Kampe de Feriet type) of general order, through which some properties have been obtained. The results obtained in this chapter include linear generating relations, differential and mixed recurrence relations, some bilateral generating relations, multiplication theorems and certain other results for the polynomial set $f_n^{(N)}[x,y]$ defined in (2.1.1). The most interesting result is the bilateral generating relation (2.3.4), which in turn, reduces to several multilinear and multilateral generating relations for Laguerre, Hermite and Legendre polynomials.

Chapter III deals with another polynomial set of the Kampe De Feriet type. We have, therein, derived linear and bilateral generating relations, multiplication theorem, differential and mixed recurrence relations and some other results for the polynomial set $g_n^{(N)}[x,y]$ defined in (3.1.1). We get many multilateral and multilinear generating relations as special cases of the bilateral generating relation (3.3.4).

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In Chapter IV, we have defined a polynomial set, which unifies amongst others, the generalized Hermite polynomial and the Euler polynomials of two variables as well as those of higher orders, defined by Nörlünd [a]. Starting from §4.3, we have attempted to deduce certain properties for our polynomial set $C_{n;\,(\mu_1);\,(\nu_1)}^{(m_1);\,(\alpha_1)}[(x_1);\,(a_1)]$ defined in (4.2.1), viz., recurrence relations, characterization, expressions in terms of other polynomials, mixed generating relations, multiplication theorem, complementary argument theorem, an integral representation etc.

The Vth and the last chapter deals with another unified polynomial set, which unifies Bernoulli polynomials, Eulerian polynomials, Hermite polynomials and their generalizations and Bernoulli polynomials of higher order defined by Norlund. In this chapter, we have made attempts to derive some properties of our polynomial set $A_{n;\,(\mu_1);\,(\nu_1)}^{(m_1);\,(\alpha_1)}[(x_1);\,(a_1);\,(c_1);\,(k_1)]$ defined in (5.2.1), viz., recurrence relations, characterization, expression in terms of other polynomials, mixed generating relation, multiplication theorem, complementary argument theorem, an integral representation etc.

INVESTIGATION ON SUMMABILITY OF TRIGONOMETRIC SERIES AND FIXED POINTS IN METRIC SPACES

Fazlul Haque Sup. : *Dr. Ashok Saxena*

The present thesis entitled "Investigation on Summability of Trigometric Series and Fixed Points In Metric Spaces" comprises seven Chapters.

In the first Chapter, which serves as an introduction to the work presented here, I have tried to give a sufficiently complete and up-to-date picture of the relevant portions of the theory.

In the second Chapter, we have generalized the theorem of A. Saxena (1965) on uniform Harmonic summability of conjugate series of a Fourier series to uniform Nörlund summability of the conjugate series of a Fourier series.

Chapter III has been divided into two parts.

In the first part, we have established a theorem concerning the Strong (L) summability of Fourier series by Nörlund means. In the

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second part, we have obtained a result for the Strong (L) summability of the derived series of a Fourier series by Nörlund means.

In Chapter IV(a) and IV(b), we have established so general theorems concerning the uniform Nörlund summability of the conjugate derived series of the Fourier series which generalize the previous result in the same direction.

In Chapter V, a theorem on Borel summability of double Fourier series has been established. This result generalizes various known results.

Chapter VI has been divided into two parts.

In the first part, we have generalized the theorem of L. M. Tripathi (1963) on the Harmonic summability of the conjugate derived series of Fourier series. We have established a theorem on the uniform matrix summability of the conjugate derived series of the Fourier series.

In the second part, we have generalized this result still further.

In the last chapter, we have obtained theorem on fixed points in complete metric spaces. The results obtained are the extensions of theorem 1 of Phulendu Das (1980) on fixed points in compact metric spaces.

A CLARS OF MODIFIED H-FUNCTIONS OF TWO VARIABLES AND THEIR APPLICATIONS

Indra Kumar Sup. *Dr. Y. N. Prasae*

In the field of Special function the H-function defined by C. Fox and H-function of two variables defined by P. K. Mittal and K. C. Gupta are well known now-a-days. The mixed Gamma function factors in the defining integrals by P, K. Mittal and K. C. Gupta are of the type

$\Gamma(a_j - \alpha_j s - A_j t)$ or $\Gamma(a_j + \alpha_j s + A_j t)$.

R. G. Buschman in a series of papers has shown that a factor of the form $\Gamma(a_j - \alpha_j s + A_j t)$ or $\Gamma(a_j \mp \alpha_j s - A_j t)$ can also be present in the integrand of the defining integral and the H-function which we have called the modified H-function of two variables will be analytic and the contour integral defining it may be convergent within sectors of s and

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t-planes. With this motivation we have defined a modified H-function of two variables and have studied it in respect of integrals, series and applications.

The present thesis deals with the modified H-function of two variables. It contains six chapters. Several integrals, series relations, a generalized polynomial quadruple integral relations and applications involving the modified H-function of two variables have been discussed.

Chapter I is introductory. It contains 5 sections in which definitions of the H-function by C. Fox and several results involving it, definitions of the H-function of two variables, the multivariable H-function, the modified H-function of two variables and a brief survey of polynomials have been given.

In Chapter II, the modified H-function of two variables has been shown to be a generating function of a polynomial namely *H-polynomial, which is assumed to be a very general polynomial. The "H-polynomial is given by

$$*H^{(n)}(x) = H^{m+1,\,l}_{p+1,\,q+1}\left[x \,\middle|\, \begin{matrix} \{(a_p, \alpha_p)\}, (n+1, 1) \\ (0, 1), \{(b_q, \beta_q)\} \end{matrix} \right]$$

$$= \sum_{r=0}^{n} \frac{(-1)^r}{\lfloor r} \frac{\prod_{1}^{m} \Gamma(b_j - \beta_j r) \prod_{1}^{l} \Gamma(1 - a_j + \alpha_j r)\, x^r}{\prod_{m+1}^{q} \Gamma(1 - b_j + \beta_j r) \prod_{l+1}^{p} \Gamma(a_j - \alpha_j r)\, \Gamma(n+1-r)}$$

provided that l, m, n, p, q are positive integers, such that $0 \leqslant l \leqslant p$, $0 \leqslant m \leqslant q$, $\alpha_j : j = 1, \ldots, p$; $\beta_j : j = 1, \ldots, q$, are positive numbers whereas $a_j : j = 1, \ldots, q$ are complex numbers, $|\arg x| < \frac{1}{2}\lambda\pi$, $\lambda > 0$, and

$$\lambda = \sum_{1}^{l} \alpha_j - \sum_{l+1}^{p} \alpha_j + \sum_{1}^{m} \beta_j - \sum_{m+1}^{q} \beta_j.$$

Other generating functions for *H-polynomial and three recurrence relations have been found. The well known polynomials have been shown to be the particular cases of our polynomial. Fourier series expansion of *H-polynomial has also been established.

Chapter III involves the infinite series for the modified H-function of two variables. Four transformation of infinite series of the modified H-function of two variables and some particular cases of it have been obtained. Further eight finite integrals involving the modified H-function of two variables and several particular cases of them have been obtained.

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Chapter IV concentrates upon some quadruple integral relations involving the modified H-function of two variables. Four quadruple integral relations involving the modified H-function of two variables and five particular cases of them have been obtained.

In Chapter V, we have evaluated six finite and infinite integrals involving the product of two modified H-functions of two variables, in the double series summation form. Seventeen particular cases of them have been derived.

Chapter VI deals with the application of the modified H-function of two-variables in 'free oscillation of water surface in a circular lake and angular twist of a bar in a shaft, we have obtained the solution of the differential equation governing the problem of free oscillation of water surface in a circular lake and angular displacement or twist of a bar in a shaft in terms of the modified H-function of two variables. Many particular cases of both have been derived. The results obtained by different authors are particular cases of the results obtained by us.

MODIFIED H-FUNCTIONS OF SEVERAL VARIABLES AND ITS APPLICATIONS

Uma Shankar Mishra Sup : *Dr. Y. N. Prasad*

The present thesis entitled "Modified H-function of several variables and its applications" is based on the modified H-function of several variales due to Y. N. Prasad and A. K. Singh, H-function of one variable due to C. Fox, H-function of two variables due to P. K. Mittal and K. C. Gupta, H-function of several variables due to H. M. Srivastava and R. Panda etc. We have given brief survey of work done by above authors in the development of these special functions. Thesis consists of six chapters.

The first chapter is introductory, the author adheres to the brief and upto date survey of the results presented by various authors and their connections to the present work. Since the author has used a new multivariable *H-function having mixed sign Gamma function factors like $\Gamma(1+2S_1-3S_2+4S_3-2S_4+\ldots+6S_r)$ in its defining integral, this *H-function, as will be seen later on, due to greater freedom in its parameters, bears away many advancement and generality on its part in comparison to Meijer's G-function, H-functions given earlier by C. Fox, P. K. Mittal and K. C. Gupta, H. M. Srivastava and R. Panda, etc.

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In Chapter II, bearing the title "Some integrals involving the modified H-function of several variables", we have evaluated finite and infinite integrals involving modified H-function of several variables. In section 2.2, we have evaluated finite integrals involving a product of Jacobi polynomial and modified *H-function of several variables. As the modified *H-function is of generalized character, a number of integrals involving these functions have been deduced. The integrals would also yield relations for Appell function, Kampe de Feriet function, Meijer's G-function etc. Expansion for the modified *H-function of several variables in a series involving the product of Jacobi polynomial and an *H-function has been obtained by using these integrals. In section 2.5, we have evaluated six finite integrals involving modified *H-function of several variables and Jacobi polynomials. In section 2.8, we have evaluated some infinite integrals involving the modified *H-function of several variables which are most general in nature and useful in solving certain boundary value problems. At the out set, we should remark that our integral formulae are quite general in character. Indeed, these results can suitably be specialized to a number of known or new integrals involving a large spectrum of special functions. The results obtained by Y. N. Prasad and A. K. Singh, O. P. Garg, A. P. Mishra etc. are particular cases of our results.

Chapter III is entitled "Fourier series and expansion formulae for the modified H-function of several variables". In section 3.2, we have evaluated Five integrals involving the modified *H-function of several variables. These integrals have been used to establish the Fourier series for the generalized *H-function. The results obtained by C. L. Kaul, Y. N. Prasad and A. Siddiqui, S. D. Bajpai, B. P. Parasar are the particular cases of our results.

We have also established four new and interesting expansion formula for this modified *H-function r-variables. These results are more general than recently obtained by Y. N. Prasad and S. Prasad.

In Chapter IV, entitled "Fractional integral operators involving the modified *H-function of several variables", we have obtained the images of the modified *H-function of several variables in these operators. Next with the help of these images we obtain four theorems showing interesting interconnections existing between the fractional integral operators of our study and the generalized *H-trans form. On account of the most general nature of our operators and the modified *H-function of several variables a number of results concerning simpler fractional integrals operators and special cases of the modified *H-function of several variables follow as particular cases of our findings.

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In Chapter V, we have obtained a general multiple transformation involving a product of two multi-variable H-functions. The transformation, which is established by using an extended Derichlet's multiple integral due to M. S. Klamkin, K. C. Gupta etc. By suitable specialization of the function occurring in the main result, some multiple integrals are also evaluated. Since our multiple integral transformation involves a product of two multivariable H-functions, we can obtain a large number of multiple integral transformation involving special functions of interest to mathematical analysts and applied Mathematicians by specializing the patameters in a suitable manner. These transformation can also be used to discuss the Derichlet's distribution of stat istics. We have also evaluated two integrals by employing the transformation.

In Chapter VI, bearing the title "Applications of modified H-function of several variables in non-linear differential equation and electric circuit theory", we move away from the analytical study of the "special functio ı" to some aspects of their applications. The literature on their various applications in a number of fields is vast, therefore, won't be given here in detail. The importance of the modified multivariable *H-function, however lies in the fact that many of the special functions occurring in the practical problems of various disciplines follow as its particular cases. Here, we concentrate ourselves mainly to obtain a solution of non-linear differential equation and the value of the charge at any time t in an electric circuit. In section 6.2, we have obtained a solution of the differential equation. The result obtained here serves as a rich source of approximate solutions of a class of non-linear differential equations-containing an exponential, a binomial, a Bessel function of first kind etc. as non-linearties. In the present section an attempt has been made to obtain a solution of the differential equation.

$$\frac{d^2x}{dt^2} + w_o{}^2 x^{\rho} * H\left[z_1 x^{\sigma}, \ldots, z_r x^{\sigma_r} \right] = 0$$

by making use of linear Jacobi polynomial approximation. Here ρ and σ_i $(i=1,\ldots,r)$ are positive integers.

We have obtained a solution of the following differential equation

$$\frac{d^2x}{dt^2} + w_o{}^2 x^{\rho} * H\left[z_1 x^{\sigma}, \ldots z_r x^{\sigma_r} \right] = 0$$

under the initial conditions

$x=A$ and $x=0$ at $t=0$

A being the amplitude of motion.

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In section 6.7, we have found a result to obtain the charge at any time t in a simple electric circuit consisting of resistance, inductance, capacitance and source of electromotive force.

ON UNSTEADY HYDROMAGNETIC LAMINAR BOUNDARY LAYER FLOWS

Uma Shanker Reddy Movva Sup : *Dr. K. Lal*

Magnetic hydrodynamics has been developed because of the astrophysical phenomena arising out of the discovery of existence of large magnetic fields in some stars and the possibilities of Magneto-hydrodynamic generators as a new source of energy. On the other hand the free convection flow is encountered in cooling of nuclear reactors or in the study of structures of stars and planets which are greatly influenced by the thermal convection in their interior hence this class of flows are very significant.

The present thesis consists of seven chapters. The first chapter is introductory. It contains the basic literature of Newtonian and non-Newtonian fluids, visco-elastic fluids, Walters model of elastico-viscous fluids, Magneto-hydrodynamics, boundary layer theory and a brief work related to this investigation.

In Chapter II an analysis of the transverse magnetic field effects on the free convective flow of an incompressible, electricaly conducting elastico-viscous fluid past an infinite non-conducting vertical plate has been carried out, for both classes of impulsive as well as uniformly accelerated motion of the plate. The magnetic lines of force are assumed to be fixed relative to the plate. Expressions for the velocity field and shearing stress are obtained by the Laplace transform technique. It is observed that the fluid velocity due to impulsive start of the plate, is always greater than due to the accelerated start in both cases of cooling and heating of the plate.

Chapter III is written in two parts. In part A, we have obtained a solution for the velocity and shearing stress for the hydromagnetic laminar flow of an elastico-viscous Walters liquid B' past an infinite porous flat plate, for both classes of impulsive as well as uniformly accelerated motion of the plate. The rolls of the magnetic field, the

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suction and the elasticity of the liquid on the velocity and shear stress have been studied. It is found that the fluid velocity increases with the increase in magnetic field. In part B an attempt has been made to study the laminar flow of an electrically conducting incompressible elastico-viscous fluid past an infinite porous flat plate, to a step function change in suction velocity, in the presence of a transverse magnetic field. An arbitrary but constant suction velocity normal to the plate is allowed prior to step change. Solutions for the velocity profile and the shearing stress are obtained. The fluid velocity decreases as the magnetic field parameter increases.

Chapter IV investigates the effect of free convection currents on unsteady hydromagnetic laminar flow of an elastico-viscous fluid (Walters liquid B') past an infinite vertical plate started impulsively from rest in its own plane. Laplace transform technique have been employed to obtain solutions for the velocity profile and shearing stress. The fluid velocity decreases as the magnetic field parameter increases, in both cases of cooling and heating of the plate.

The effect of a transverse magnetic field on the unsteady flow of an incompressible, electrically conducting elastico-viscous fluid past an infinite horizontal plate started impulsively has been studied in Chapter V. Solutions to equations governing the flow are derived with the help of the Laplace transform technique. It is observed that the fluid velocity increases with the increase in the elasticity of the liquid.

In Chapter VI, unsteady hydromagnetic free convection flow of an incompressible viscous fluid past an infinite vertical porous limiting surface, which is subjected to a constant suction velocity and heat sources has been analysed at small magnetic Reynolds number, when the free stream velocity oscillates in time about a constant mean value. A perturbation solution is sought for obtaining the expressions for velocity and temperature. The results are discussed with the aid of graphs and tables.

In Chapter VII an attempt has been made to study the effect of Hall currents on oscillatory MHD boundary layer flow past an infinite porous flat plate at small magnetic Reynolds number. It is found that an increase in Hall parameter leads to a decrease in the fluctuating part of the primary flow.

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SOME DISTRIBUTIONAL TRANSFORMATIONS

Ram Kishore Pandey Sup : *Dr. R. S. Pathak*

In Chapter 1, a classical Weber transformation has been extended to a space of generalized functions. For this a theorem due to Titchmarsh which gives precise conditions of the inversion of the Weber transform, has been established. Suitable testing function space is framed. It has been shown that the Weber transform F (y) under consideration is a differentiable function of y for all $y>0$. Asymptotic orders of F(y) for large and small y are also obtained. Finally an inversion theorem is proved and the theory thus developed has been applied to solve differential operator equation and Dirichlet problem in cylindrical coordinates for a plate.

In Chapter 2, the classical Mehler-Fock transformation has been extended to distributions. A theorem due to Braaksma and Meulenbeld in which conditions for the inversion of Mehler-Fock transformation, are provided, has been extended to distribution. It has been accomplished by defining the testing function space $M_{\beta}^{\alpha}(I)$ and the distributional Mehler—Fock transformation F (r). It has been shown that F (r) is differential for $r \geqslant 0$. Orders of F(r) for large and small values of r are obtained. At the end of the chapter an operational calculus is developed to solve a certain boundary value problem.

In Chapter 3, a theorem of Hardy and Titchmarsh has been extended to distributions. Author has shown that the theorem is valid when the convergence is interpreted in the weak topology of suitable testing function space. At the end of this chapter an inversion theorem for the Hankel transform has been obtained as a special case of the extended theorem of Hardy and Titchmarsh.

MULTIVARIABLES H-FUNCTIONS AS KERNELS OF GENERALIZED INTEGRAL TRANSFORMS AND THEIR APPLICATIONS

Ram Narain Sup. : *Dr. Y. N. Prasad*

In the field of special functions, the H-function defined by C. Fox, H-function of two variables defined by P. K. Mittal and K. C. Gupta and H-function of several complex variables defined by H. M. Srivastava and R. Panda are well known now a days.

The present thesis deals with the multivariable H-functions as kernels of generalized integral transforms and their applications. It

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contains six chapters. Several integrals, theorems, integral representations for Whittaker and Hankel transforms, expansion formulae and applications in the temperature distribution in a non-homogeneous moving bodies have been discussed.

We have used the series expansion formula of the multivariable H-function which can be established with the help of the results given by R. K. Saxena, and S. N. Mukherjee and Y. N. Prasad as follows :

$$o, o : (1, n'); \ldots; (1, n^{(\gamma)}) \qquad \left[\begin{matrix} (e_j;\ E'_j, \ldots, E^{(\gamma)}_j)_{1,P} : \\ (f_j;\ F'_j, \ldots, F^{(\gamma)}_j)_{1,Q} : \end{matrix} \right.$$

$$H_{P,Q}: [p', q'+1]; \ldots; [p^{(\gamma)}, q^{(\gamma)}+1]$$

$$\left. \begin{matrix} (g'_j, G'_j)_1, p'; \ldots (g^{(\gamma)}_j,\ G^{(\gamma)}_j)_1, p^{(\gamma)} \\ (h'_o, H'_o), (h'_j, H'_j)_1, q'; \ldots; (h^{(\gamma)}_o, H^{(\gamma)}_o), (h^{(\gamma)}_j,\ H^{(\gamma)}_j)_1, q^{(\gamma)} \end{matrix} \right| \begin{matrix} \sigma \\ \xi_1 (sx)^{\iota} \\ \sigma \\ \xi_r (sx)^{\gamma} \end{matrix} \Bigg]$$

$$= \frac{1}{\prod_{i=1}^{r} \pi H^{(i)}_o} \sum_{\nu_1, \ldots, \nu_r = o}^{\infty} \phi(\rho\nu_1, , \ldots \rho\nu_r) \prod_{i=1}^{r} \left\{ \theta_i(\rho\nu_i) \frac{(-1)^{\nu i}}{\nu_i \mid} (\xi_i)^{\rho\nu_i} \quad (sx)^{\sigma_i \rho_i} \right\},$$

where

$$\rho\nu_i = \frac{h^{(i)}_o + \nu_i}{H^{(i)}_o},$$

$$\theta_i(\rho\nu_i) = \frac{\prod_{j=1}^{n^{(i)}} \Gamma(1 - g^{(i)}_j + G^{(i)}_j \rho\nu_i)}{\prod_{j=1}^{q^{(i)}} \Gamma(1 - h^{(i)}_j + H^{(i)}_j \rho\nu_i) \prod_{j=n^{(i)}+1}^{p^{(i)}} \Gamma(g^{(i)}_j - G^{(i)}_j \rho\nu_i)}$$

and

$$\phi(\rho\nu_1, \ldots, \rho\nu_r) = \left[\prod_{j=1}^{P} \Gamma(e_j - \sum_{i=1}^{r} (E^{(i)}_j \rho\nu_i)) \right]^{-1} \left[\prod_{j=1}^{Q} \Gamma(1 - f_j + \sum_{i=1}^{r} (F^{(i)}_j \rho\nu_i)) \right]^{-1},$$

provided that certain set of conditions are satisfied.

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Chapter I is introductory. In Chapter II, we have defined a new generalized integral transform involving a product of two multivariable H-functions as kernel as follows :

$$\phi(s)=\overset{\infty}{\underset{0}{\sim}} K(s, x)\, f(x)\, dx \equiv \Omega[f(x)] \qquad \text{(denote)},$$

where K(s, x), is the kernel of the integral transform, is defined by

$$K(s, x)=(sx)^{\rho-1}\,{}^{(1)}H\left[\xi_1 (sx)^{\sigma 1}, \ldots, \xi_r (sx)^{\sigma r}\right]$$
$$\qquad {}^{(2)}H[z_1 (sx)^{\mu_1}, \ldots, z_r (sx)^{\mu r}],$$

where

$$^{(1)}H\left[\xi_1(sx)^{\sigma 1}, \ldots, \xi_r (sx)^{\sigma r}\right]$$
$$=H^{o,o:(1,n');\ldots;(1,n^{(y)})}_{P,Q:[p',q'+1];\ldots;[p^{(y)},q^{(y)}+1]}\left[\begin{matrix}(e_j;E_j', \ldots, E_j^{(y)})_{1,P} : (g_j', G_j')_{1,p'};\ldots;(g_j^{(y)}, G_j^{(y)})_{1,p^{(y)}} \\ (f_j; F_j', \ldots F_j^{(y)})_{1,Q} : (h_o', H_o'), (h_j', H_j')_{1,q'};\ldots; \\ (h_o^{(y)}, H_o^{(y)}), (h_j^{(r)}, H_j^{(y)})_{1,q^{(y)}} \end{matrix}\middle| \begin{matrix}\xi_1 (sx)^{\sigma 1} \\ \vdots \\ \xi_y (sx)^{\sigma 1}\end{matrix}\right]$$

and

$$^{(2)}H\left[z_1 (sx)^{\mu_1}, \ldots, z_r (sx)^{\mu_r}\right]$$
$$=H^{o,o:(M',N');\ldots;(M^{(y)},N^{(y)})}_{p,q:[p',Q'];\ldots;[p^{(y)},Q^{(y)}]}\left[\begin{matrix}\{(a_p;(\alpha_p^{(i)})_{i=1,\ldots,r}\}: \\ \{(b_q;(\beta_q^{(i)})_{i=1,\ldots,r}\}:\end{matrix}\right.$$
$$\left.\begin{matrix}\{(c_{p'}', \gamma_{p'}')\};\ldots;\{(c_{p(y)}^{(y)}, \gamma_{p(y)}^{(y)})\} \\ \{(d_{Q'}', \delta_{Q'}')\};\ldots;\{(d_{Q(y)}^{(y)}, \delta_{Q(y)}^{(y)})\}\end{matrix}\right| \begin{matrix}z_1 (sx)^{\mu_r} \\ \vdots \\ z_r (sx)^{\mu_r}\end{matrix}\Bigg]$$

with certain restrictions on the parameters. Several specializations of this Ω—transform studied by various authors have been derived. An inversion theorem followed by an illustrative example has also been given. Lastly we have given numerous basic properties enjoyed by this Ω—transform defined by us.

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In Chapter III, we have given the chain properties enjoyed by this Ω—transform with various other well known integral transforms such as Whittaker transform, Hankel transform, Laplace transform, Y_ν—and H_ν—transforms defined by E. C. Titchmarsh etc. The results have been classified by means of eight theorems followed by illustrative examples.

In Chapter IV, we have given the generalizations of Whittaker transform, Hankel transform and Laplace transform in the form

$$W-\Omega\,[f(x)] = \underset{o}{\overset{\infty}{\sim}} (sx)^{\rho-1} e^{-\frac{1}{2}sx}\, W_{k,m}(sx)$$

$$(1)H\,[\xi_1\,(sx)^{\sigma 1},\ldots,\xi_r\,(sx)^{\sigma r}]$$

$$(2)H\,[z_1\,(sx)^{\mu 1},\ldots,z_r\,(sx)^{\mu r}]\; f(x)dx.$$

$$H-\Omega[f(x)] = \underset{o}{\overset{\infty}{\sim}} (sx)^{\frac{1}{2}}\, J_\nu\,(sx) \quad (1)H\,[\xi_1\,(sx)^{\sigma 1},\ldots,\xi_r(sx)^{\sigma r}]$$

$$(2)H\,[z_1\,(sx)^{\mu 1},\ldots,z_r(sx)^{\mu r}]\; f(x)dx$$

and

$$\mathcal{L}-\Omega[f(x)] = \underset{o}{\overset{\infty}{\sim}} e^{-sx}\; (1)H\,[\xi_1\,(sx)^{\sigma 1},\ldots,\xi_r(sx)^{\sigma r}]$$

$$(2)H\,[z_1\,(sx^{\mu_1},\ldots,z_r(sx)^{\mu r}]\; f(x)\,dx.$$

We have given the integral representations for these generalizations in the form of seven theorems where each theorem is followed by the illustrative examples.

In Chapter V, we have evaluated some finite and infinite integrals involving the multivariable H-functions. We have next given an expansion formula for the product of multivariable H-functions in the series of Jacobi polynomials. The generalizations of the integrals and expansion formula have been discussed briefly.

Chapter VI deals with the applications of the H-functions of r-variables in the temperature distribution in a non-homogeneous moving plate and parallelopiped.

For instance we have considered a non-homogeneous plate of bredth b, thermal conductivity proportional to $(1-x^2)$ and moving with a variable velocity proportional to $[\alpha-\beta+\gamma+(\alpha+\beta-\gamma)x]$,($\alpha,\beta,\gamma$ being constants), in the direction of its length (x-axis) between the limits $x=-1$ to $x=1$. Now we have supposed that the edges $y=O$, $y=b$ of the plate and the two ends $x=\pm 1$ are insulated.

The H. S. Carslaw and J. C. Jaeger have given the differential equation satisfied by the temperature $\theta(x,y,t)$ at any time t in a homo-

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geneous plate with conductivity K, density ρ, specific heat c, diffusivity k and moving with uniform velocity u in the direction of its length, αs

$$k\left(\frac{\partial^2\theta}{\partial x^2}+\frac{\partial^2\theta}{\partial y^2}\right)-u\frac{\partial\theta}{\partial x}-\frac{\partial\theta}{\partial t}=0. \qquad k=\frac{K}{\rho c},$$

The above differential equation in our suppositions reduces to

$$\frac{\partial\theta}{\partial t}=k_0\left[(1-x^2)\frac{\partial^2\theta}{\partial x^2}+\left\{\beta-\alpha-\gamma-(\alpha-\gamma+\beta+2)\,x\right\}\frac{\partial\theta}{\partial x}+k\frac{\partial^2\theta}{\partial y^2}\right.$$

where $k_0=k'/\rho c$, $Re(\alpha)>-1$, $Re(\beta)>\gamma-1$, In our case the conductivity is supposed to be $k'(1-x^2)$ and velocity $k_0[\alpha+\gamma-\beta+(\alpha-\gamma+\beta)x]$.

Now according to our assumption no heat flows from the edges $y=0$, $y=b$ and the boundary conditions, therefore, for the problem are

$$\frac{\partial\theta}{\partial y}=0 \text{ at } y=0 \text{ and } y=b.$$

We also assume the initial temperature distribution in the plate to be

$$\theta(x, y, 0)=f(x, y)=f_1(x)\,f^2(y)$$

where

$$f_1(x)=(1-x)^{\rho}(1+x)^{\sigma}$$

$$^{(1)}H[\xi_1(1-x)^{\sigma_1}\ (1+x)^{\rho_1},\ldots,\xi_r(1-x)^{\sigma_r}\ (1+x)^{\rho_r}]$$

$$^{(2)}H[z_1(1-x)^{\delta_1}(1+x)^{\mu_1},\ldots,z_r(1-x)^{\delta_r}(1+x)^{\mu_r}]$$

$$f_2(y)=e^{-\mu y},\ \mu>0.$$

In this way, we have obtained the most general solution of the above differential equation which is believed to appear for the first time in the literature. Several particular cases have also been discussed.

CERTAIN INVESTIGATIONS IN RECURRENT FINSLER MANIFOLDS

Gulab Singh Sup : *Dr. B. B. Sinha*

The thesis entitled "certain investigations in recurrent Finsler manifolds" consists of five chapters.

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In Chapter I entitled "Finsler manifolds" we have studied linear frame bundle, tangent bundle, Finsler bundle, Cartan, Rund, Berwald and Hashiguchi connections and Lie derivatives and their properties.

In Chapter II entitled "Recurrent neo-pseudo projective curvature tensor field" we have studied neo-pseudo projective curvature tensor field and recurrent neo-pseudo projective curvature tensor field in Finsler manifold of first and second order and the properties of recurrence vector and tensor fields. We have also studied the neo-pseudo projective curvature tensor field of Finsler manifold of scalar curvature.

In Chapter III entitled, "Recurrent curvature tensor fields of order r" we have studied recurrent normal projective Finsler manifold and recurrent neo-pseudo projective Finsler manifold of order r. Certain properties of recurrence tensor field, normal projective curvature tensor field and neo-pseudo projective curvature tensor field in recurrent Finsler manifold of order r have been investigated.

Chapter IV bears the title "Decompositions of recurrent curvature tensor field". In this chapter we have studied decompositions of neo-pseudo projective curvature tensor field in a non Q-flat (neo-pseudo-projective curvature tensor field $Q^{i}_{jkh} = O$) Finsler manifold. In an n-dimensional non Q-flat Finsler manifold out of six types of decompositions is only one decomposition possible and the neo-pseudo projective curvature tensor field of an isotropic Finsler manifold F_n $(n>2)$ could not be decomposed. We have also studied the decomposition of neo-pseudo projective curvature tensor field in Q-recurrent Finsler manifold of second order.

In Chapter V entitled, "Motions in recurrent Finsler manifolds" we have studied an affine motion and certain types of projective motions in recurrent neo-pseudo projective Finsler manifold of a non-zero scalar curvature and special concircular transformation in neo-pseudo projective Finsler manifold. The special infinitesimal conformal motion contra and concurrent conformal motion in recurrent Finsler manifold have been dealt with in this chapter.

A selected list of the books and research papers which have been consulted during the preparation of the work is given in the end.

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SOME STUDIES IN HOMOGENEOUS COSMOLOGIES IN GENERAL RELATIVITY

Jagdish Prasad Singh Sup ; *Dr. S. R. Roy*

The thesis entitled "Some Studies in Homogeneous and Inhomogeneous Cosmologies in General Relativity" comprises six chapters. Each chapter has been divided into four sections. The first section of each chapter is introductory in nature and it contains well known results which are essential for subsequent investigations.

Chapter I is entitled "Some Homogeneous Viscous Fluid Cosmological Models". The first section of this chapter is a brief survey of some well known homogeneous cosmological models. The remaining portion of the chapter deals with Bianchi type VI_h space-times representing viscous fluid distribution and their physical consequences. We have derived a number of exact solutions of Einstein's field equations which represent different eras in the evolution of the Universe. A particular solution of Bianchi type V space-time satisfying barotropic equation of state has also been obtained. Some physical features of the models have been studied. In one of the models the effect of viscosity on the horizon structure has also been investigated.

In Chapter II entitled "Bianchi Type I Cosmological Models with Perfect Fluid and Magnetic Field" we have obtained a number of cosmological models containing perfect fluid and source free magnetic field. The first model represents stiff fluid distribution while in the rest of the models the volume expansion θ has been taken to be a linear combination of the eigen values of the shear tensor σ_{ij}. This condition is a generalisation of the condition $\sigma/\theta = \text{constant}$. Physical consequences of the field equations have been discussed. Taking the present day values of Hubble parameter H_0 to be 75 km. sec^{-1} Mpc^{-1}, matter density $\epsilon_0 = 5 \times 10^{-30}$ gm cm^{-3} magnetic energy density $\rho_0 = 5 \times 10^{-35}$ gm cm^{-3} and present day observed anisotropy σ_0/θ_0 of the microwave background radiation to be 10^{-3}, it is found that the present day value of deceleration parameter $q_0 = -0.3$ and cosmological constant $\Lambda = -9.4 \times 10^{-35}$ sec^{-2}. Various physical features of the models have been studied.

Chapter III is entitled "Bianchi Type VI_0 Perfect Fluid Cosmological Models with Magnetic Field". In this chapter cosmological models of perfect fluid distribution with source free magnetic field have been derived by using the supplementary condition that the volume expansion θ is a linear combination of shear eigen values which in turn

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reduces to $\sigma/\theta = \text{constant}$ for the given distribution. Present day value of deceleration parameter q_o is found to be 0.24 for $\Lambda = 0$. However for $q_o = 1$ cosmological constant $\Lambda = 1.36 \times 10^{-35}$ sec^{-2}. Various physical features of the models have been discussed. In two of the models present age T_o of the Universe is estimated to be H_o^{-1} i.e. 1.3×10^{10} years and cosmological constant $\Lambda = -6.07 \times 10^{-36}$ sec^{-2}. It is found that in one of the models, the matter distribution reduces to that of a pressureless fluid in the absence of cosmological constant while in another model the presence of magnetic field removes the possibility of a singularity

Chapter IV entitled "Some Bianchi Type VI_o Cosmological Models with Free Gravitational Field of the 'Magnetic' Type" deals with Bianchi type VI_o space-time with the adhoc condition that the free gravitational field is of the 'magnetic' type while the matter distribution is a viscous fluid with an incident magnetic field. It is found that the 'magnetic' part of the free gravitational field induces shear in the fluid flow which is zero in the case of a gravitational field of purely 'electric' type. It is also found from the geodesic deviation equation that the free gravitational field does not affect the relative motion pattern of the fluid flows. Some exact solutions of the field equations have been derived and physical features of the models have been discussed.

In Chapter V entitled "LRS Bianchi Type V Universes Filled with Matter and Radiation", we have examined the possibility of a source free electromagnetic field coexisting with matter in the form of a viscous fluid and streaming neutrinos in the case of LRS (locally rotationally symmetric) Bianchi type V universes. It is found that the shear viscosity is incompatible with such a Universe in the absence of streaming neutrinos. The electromagnetic field is necessarily null and its effect is to introduce a non-vanishing shear in the fluid flow. We have derived a number of exact solutions and discussed the physical and kinematical features of these models. Present day value of the electromagnetic energy density has been estimated to be 5.0×10^{-32} gm cm^{-3}.

Chapter VI entitled "Some Inhomogeneous Viscous Fluid Cosmological Models in General Relativity" contains a brief description of inhomogeneous cosmology and well known inhomogeneous cosmological models in its first section. In the remaining sections some cosmological models of Szekeres type corresponding to a viscous fluid distribution have been obtained. Various physical features of these models have been discussed.

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ON UNSTEADY BOUNDARY LAYER

Janardan Singh Sup. : *Dr. K. Lal*

The subject of unsteady boundary layer has been studied by Engineers and Geophysicists for many years. It has its application in several fields of technology, e.g. Petroleum engineering, agriculture engineering, chemical engineering and soil mechanics etc. Still, many investigations are to be carried out on fluid flows in boundary layer for practical applications.

It consists of seven chapters. Chapter I is general introduction which describes the brief introduction, the basic equations, the definition of several physical parameters and the relevant literature connected with unsteady boundary layer.

In Chapter II, we have studied the mass transfer effect on the free—convection flow of an incompressible viscous fluid past a uniformly accelerated infinite vertical plate by assuming constant heat flux between fluid and plate. The expression for the velocity field and skin friction have been obtained by the Laplace transform techniqee. The influence of the various parameters entering into the problem is extensively discussed with the help of graphs and tables. The contents of the chapter is under publication in Astrophysics and space science.

Chapter III deals with the flow of an incompressible, viscous and electrically conducting fluid through a porous medium due to an uniformly accelerated porous plate. The Laplace transform has been used to find out the expression for velocity field and from this skin-friction at the plate is calculated. The variations of velocity and skin frictions are discussed with the help of graphs and tables. Case I of this chapter has been accepted in Institute of Theoretical Physics and Case II has been accepted in Journal of Scientific Research.

Chapter IV investigates Hydromagnetic flow of an elastico-viscous fluids past an accelerated plate when the magnetic lines of forces are fixed relative to the plate. The expression for velocity profiles and skin friction are obtained by the Laplace transform method. The variations of velocity profiles and skin friction have been shown by graphs and table. The contents of the chapter has been accepted for publication in National Academy of Science letter.

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In Chapter V, a theoretical analysis of the two dimensional flow of an incompressible viscous electrically conducting fluid through a porous medium bounded by porous plate is presented. The suction velocity perpendicular to the plate fluctuates in magnitude but not indirection about a non-zero constant mean. The mathematical analysis is presented for the hydromagnetic boundary layer flow without taking into account the induced magnetic field. The effects of porous medium and strength of magnetic field on the skin friction phase and amplitude are shown graphically. The contents of the chapter has been accepted for publication in Journal of Scientific Research.

Chapter VI presents the flow of an incompressible and electrically conducting fluid due to accelerated motion of an infinite porous plate with constant suction at the plate. Expression for the velocity field and induced magnetic field have been obtained by Laplace transform method when the magnetic Prandtl number is unity. Variations of velocity profiles and induced magnetic field have been shown by graphs while the numerical values of skin-friction and current density have been entered in table.

In Chapter VII the flow of an elastico-viscous fluid (Walters liquid B^1) is analised due to uniformly accelerated motion of an infinite porous plate which is subjected to a constant suction. It is found that at a fixed time, the velocity at any point decreases as the suction velocity at any point or elasticity of the fluid increases. The skin friction decreases as suction velocity increases but increases as elastic parameter increases.

HYDRODYNAMIC DISPERSION IN UNSTEADY FLOW THROUGH POROUS MEDIA

Naveen Kumar Singh Sup : *Dr. K. Lal*

Porous materials are encountered literally everywhere in everyday life, in technology, and in nature, with the exception of metals, some dense rocks, and some plastics. The unique property of porous medium that distinguishes it from other solids on the one hand, and from simple conduits on the other, is its complicated interconnected three-dimensio-

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nal network of capillary channels of nonuniform sizes and shapes, commonly referred to as 'pores'. There have been numerous attempts over the past fifty years or so to explain the flow phenomena, diffusion, dispersion, and electrical conduction in porous media in terms of microscopic structure as accurately as possible. The results have seldom been entirely satisfactory. So most of the brilliant and successful practitioners in this field have tried as much as possible, to stick with the continuum approach in which no attention is paid to pore structure.

The first chapter introduces the subject and its applications in different branches of science and technology. First porous media is defined and some examples are given. Continuum approach is discussed for the discription of porous media and flow model through it. The basic parameters porosity, permeability along with hydrodynamic dispersion phenomena and the governing differential equations stating concentration distribution, are given in brief. In the last section the summary of some important works related with this topic has also been given. The chapter concludes with the theme of the present thesis.

Chapter two deals with the dispersion problem in a finite, homogeneous and isotropic porous medium. Dispersion is controlled by the unidirectional, unsteady flow of a low concentration fluid towards a region of higher concentration. Seepage velocity is varying exponentially with time. An exponential function concentration is enforced at the source of the dispersion, while zero concentration, or a condition in which the change in concentration is proportional to the flow, is applied at the other boundary. To solve this problem, the relationship that the dispersion coefficient is almost proportional to the product of the seepage velocity and the particle diameter, is used. This proportionality extends over a broad range of Reynolds number ($=ud\rho/\mu$, where u is the seepage velocity, d is the particle size diameter of porous matrix, μ is dynamic viscosity and ρ is the density) upto 100. Further a new time variable has been also introduced. Laplace transform technique is used for solving the unsteady dispersion problems for nonadsorbing as well as for adsorbing porous media. Alternative solutions are obtained for smaller or larger values of time. The results for the contaminant concentration distribution in a nonadsorbing porous medium are computed for the input parameters values and are plotted in the respective figures. Figures show that at smaller times the concentration distribution at the other boundary is zero while at larger times, some concentrations occur as dictated by the second set of boundary condition.

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Chapter three presents analytic solutions for the dispersion of a solute in a semi-infinite, homogeneous as well as isotropic porous medium. Porous medium is taken nonadsorbing and adsorbing both. Horizontal flow through it is governed by the seepage velocity varying exponentially with time. Two types of input concentrations varying exponentially with time are chosen to form two sets of initial and boundary conditions. Taking the advantage of direct relationship of dispersion coefficient with seepage velocity and introduction of new time variable, the concerned differential equations along with a set of initial and boundary conditions, are solved using Laplace transform technique. The results are computed and shown in the figures. For adsorbing porous medium, the concentration distribution at a time and at a particular position is less than that for nonadsorbing porous medium,

Chapter four investigates the longitudinal dispersion problem analytically in a semi-infinite granular medium which is first taken nonadsorbing and then adsorbing one. Flow through it is defined as seepage velocity varying inversely proportional to square root of time variable. The input concentration varies directly with time. The same procedure as in previous chapters is adopted in getting the solutions.

Chapter five formulates mathematically the salinity intrusion problems in the coastal and tidal regions. A freshwater and saltwater system is supposed in a test column which contains a porous medium upto certain length with the special characteristic of adsorption. The unsteady movement of sharp interface separating the two liquids, is defined by exponential and oscillatory form of seepage velocity respectively. The input concentration increases exponentially with distance in the former case, while decreases exponentially with distance in the latter case. The dispersion problem with first form of seepage velocity is solved analytically and by finite-difference implicit method and the results are shown graphically which show excellent agreement between the two results. Considering oscillatory form of velocity second method is used to get the results which show the oscillatory distribution of concentration distribution in the figure.

Chapter six illustrates the computed values of concentration distribution in unsteady seepage flow through inhomogeneous porous media for three different one-dimensional dispersion systems respectively

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as well as the porosity variation with the horizontal coordinate which is the cause of inhomogeneity of the porous media. Two such porosity functions are taken. The first dispersion system has the input concentration increasing exponentially with distance, second dispersion system allowing dispersion to occur against the unsteady flow, whereas the third system demands continuous concentration distribution to occur at the other boundary also. The implicit finite-difference method is applied in getting the results. The accuracy of the results is judged by comparing the results with those for the homogeneous porous media which have been obtained in previous chapters.

Chapter seven elucidates the unsteady velocity distribution and solute concentration distribution in a porous channel which is bounded on its both sides by permeable matters having somewhat less permeation capability. At the boundaries of the flow system slip conditions are assumed such that the slip velocity is proportional to the exterior velocity gradient, to replace the effect of boundary layer. Two alternative results for unsteady velocity distribution are obtained. The Aris method is used to get the result that the rate of change of concentration distribution variance will be proportional to the dispersion coefficient when the seepage velocity will be considered unsteady.

SOME PROBLEMS ON DISPERSION IN POROUS MEDIA FLOW

Rajendra Singh Sup. : *Dr. K. Lal*

Hydrodynamic dispersion problems have its application in many fields of technology, for example, in chemical, petroleum and oil reservoir engineering, ground water hydrology and soil mechanics etc. It's subject has been studied by the Geophysicists and engineers. There remains much more investigations on fluid flow in porous media for practical applications. To predict the moment of possible contaminants in a porous media flow, one may either use closed-form solutions or rely on numerical solutions. Analytical solutions for some dispersion problems are presented in this thesis, which are most economical and efficient in application and they also provide a simple tool for understanding the relative importance of the various parameters. The Laplace

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transform technique has been used while developing the analytical solutions. The expressions, stating the behaviour of concentration distribution throughout the porous medium, are computed for certain set of data in different chapters.

The thesis consists of seven chapters. The first chapter contains the general introduction of the subject. The basic equations of several variables connected with flows in porous media are given in this chapter. Besides these, several papers written by various authors have been given in brief. These papers have interconnection with my contribution, which have been given in Chapters 2-7, of the thesis.

In Chapter 2, analytical solutions are developed for the distribution of contominants within an adsorbing porous medium with and without radioactive decay, in a unidirectional flow field, subject to a input concentration that varies exponentially and trigonometrically with time. The medium is considered to be homogeneous, isotropic and semi-infinite. The average velocities are considered constant throughout the flow fields. In addition, solute transport is influenced by hydrodynamic dispersion as well as by ion-exchange equilibrium. Results have been given by graph and tables. It is concluded that the radioactive decay is responsible for less concentration in liquid matrix at any time than that without this effect.

Chapter 3, investigates the solutions for concentration as a function of time and space in non-adsorbing porous media. The effect of radioactive decay is also taken into account. The medium under consideration is isotropic, homogeneous and semi-infinite. The flow is unidirectional and average velocities are constant throughout the flow field. The input concentration here is $C_o t^m e^{wt}$, where C_o is reference concentration, $m \geq O$ and w is positive or negative. Solutions for $m = O$, 1,2 and $w = O$, -1/min are presented in both parts. Results have been given by graphs and tables. The solutions are useful for solving representative field problems.

In Chapter 4, the mathematical solutions for dispersion problem within a saturated granular medium, in a unidirectional flow field, are derived. Here, the concentration of the displacing fluid is an algebric function of time. The medium is homogeneous, isotropic and finite in real extent. Analytical solutions are developed for adsorbing and non-adsorbing medium. Graphical solution is given for non-adsorbing

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case, while table is given for adsorbing medium case. By comparing the graph and table, we concluded that the concentration distribution at any time in the liquid phase is less in the adsorbing porous media than that in the non-adsorbing porous media. The solutions developed are useful for other process such as decay of organic substance and radioactive decay.

Chapter 5, deals with the distribution of contaminants within an adsorbing and non-adsorbing porous medium, with and without radioactive decay in a unidirectional flow field, subject to trigonometrical function for input concentration. The medium is homogeneous and finite in real extent. The solutions predict the concentration of contaminants as a trigonometrical function of time and space, if the seepage flow, adsorption and dispersion coefficients are prescribed. Graphical solutions are presented for some cases and tables are given for others. From the two illustrations, it is seen that the effect of radioactive decay in adsorbing porous media causes more less concentration in liquid matrix than that in non-adsorbing one. The models are useful for predicting the concentration of contaminants in representative field problems.

In Chapter 6, longitudinal dispersion has been discussed for steady uniform laminor flow through porous media. Periodic solution is obtained for concentration distribution. Results are given by graph and table. The solution predicts the distribution of contaminants resulting from the variable source concentration. They should prove useful in analyzing the possible contaminants of ground water resulting from seepage of high salt concentration in drainage, ditches and canals.

Flow against dispersion in a finite adsorbing and non-adsorbing porous media is studied in Chapter 7. Concentration varying as algebric function of time is enforced at the source of dispersion, while a condition in which the change in concentration is proportional to the flow is applied at the other boundary. It has been concluded that concentration increases as distance increases, when time is kept constant. The solutions are useful for quantitatively predicting the possible control of spreading of poor quality water by fresh water.

In the end of the thesis, 'Bibliography' is given which includes a large number of references of which I got valuble help consulted most of them.

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CERTAIN INVESTIGATIONS IN DIFFERENTIABLE MANIFOLDS

Ram Nawal Singh Sup : *Dr. B. B. Sinha*

The thesis entitled "Certain Investigations in differentiable manifolds" comprises six chapters. Each chapter has been divided into sections. The first chapter is introductory in which the concepts of differentiable manifold, tangent space, connexions, co-variant derivatives, Lie derivatives Riemannian manifold and its submanifolds have been developed The important properties of Riemannian manifold and its submanifold have also been given. This chapter also deals with the structures on differentiable manifolds, such as almost complex manifold, almost Hermite manifold, almost Kahler manifold, Kahler manifold, almost contact manifold, Sasakian manifold, almost product manifold, almost paracontact manifold, para-Sasakian manifold, Almost hyperbolic Hermite manifold, almost hyperbolic Kahler manifold, hyperbolic Kahler manifold, hyperbolic contact manifold and hyperbolic Sasakian manifold. Since these structures are studied widely so only those portions have been touched which have been used in the sequel.

The Chapter II entitled "Curvature of Holomorphically Semi-Symmetric Connexions" is divided into two sections. In the first section we have studied holomorphically semi-symmetric connexion $\tilde{D}$ which was first studied by Prvanovic (1979). If S be the torsion tensor of the connexion $\tilde{D}$, then we have established that in Kahler manifold

$$2\tilde{D}_X Y - \overline{S(\bar{X}, Y)} + S(X, Y), F(X) = \bar{X}$$

is invariant of holomoaphically semi-symmetric change. Also, we have defined holomorphically semi-symmetric curvature tensor H in Kahler manifold which is invariant of holomorphically semi-symmetric change and have studied some properties of this curvature tensor. In the second section we have obtained similar results in hyperbolic Kahler manifold.

The Chapter III entitled "Quarter Symmetric Connexions" was first defined by Golab (1975). In the first section we have defined quarter symmetric metric connexion in a Riemannian manifold. In the second section quarter symmetric metric connexion has been studied in an almost paracontact metric manifold. In third section, it has been established that if the quarter symmetric metric connexion be special quarter symmetric metric connexion, that is, the 1-form p be gradient then the curvature tensors of special quarter symmetric metric connexion and a Riemannian connexion, coincide in hyperbolic Kahler manifold. In the

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fourth section, we have obtained the necessary and sufficient condition for a hyperbolic Sasakian manifold M^n admitting a quarter symmetric metric connexion with vanishing curvature to be flat. In the fifth section, we have defined another quarter symmetric metric connexion in hyperbolic Kahler manifold. We have proved that if a hyperbolic Kahler manifold M^n admitting a quarter symmetric metric connexion with respect to which the curvature tensor vanishes, then the manifold is conharmonically flat if and only if the manifold is of zero scalar curvature. In the last section another quarter symmetric metric connexion has been studied in an almost contact metric manifold.

The chapter IV entitled "Conformal Infinitesimal Transformations" is divided into two sections. In the first section, we have obtained the necessary and sufficient condition for a vector field U to be conformal infinitesimal transformation in an almost paracontact metric manifold. We have also proved that if a vector field U is a conformal infinitesimal transformation of a compact almost paracontact metric manifold M^n with (F, A, T, g) structure, provided g (T, [T, U]) has a fixed sign, then U is an infinitesimal automorphism. In the second section, we have studied the conformal infinitesimal transformations in hyperbolic contact metric manifold. We have proved that in an almost hyperbolic Sasakian manifold M^n, every conformal infinitesimal transformation U is an automorphism.

The Chapter V entitled "Submanifolds" has been divided into four sections. In the first and second sections we have studied the hypersurfaces with hyperbolic (f, g, u, v, λ) structure of hyperbolic contact and hyperbolic cosymplectic metric manifolds. In third section umbilic and normality conditions of hyperbolic (f, g, u, v, λ) structure have been studied. In the fourth section, we have defined framed hyperbolic f-manifold M^{n-s} whose particular cases are almost product manifold and hyperbolic contact manifold. We have obtained the necessary and sufficient conditions for the submanifold M^{n-s} with hyperbolic structure (f, u_x, u_x, g) of an almost hyperbolic Hermite manifold M^n to be framed hyperbolic metric submanifold. We have proved that a framed hyperbolic metric submanifold M^{n-s} be normal if and only if M^{n-s} is framed hyperbolic pseudo umbilical submanifold.

The Chapter VI entitled "Infinitesimal Normal Variation" has been divided into two sections. In the first section hypersurfaces with hyperbolic quartic structure (f, u, v, U, V) of hyperbolic cosymplectic manifold have been studied. We have proved that if the hyperbolic quartic structure on the non-invariant hypersurface of a hyperbolic

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cosymplectic manifold is normal and f be parallel, the manifold is flat and the structure tensors f, u, v, U, V are covariant constant. In second section, the variations of structure tensors f, u, v, U, V are obtained under infinitesimal normal variation. We have proved that if the hyperbolic quartic structure on the hypersurface of a hyperbolic cosymplectic manifold be normal and f be parallel, then structure tensors are invariant under infinitesimal normal variation.

SOME ASPECTS OF HEAT AND MASS TRANSFER IN MHD FLOWS

Vijayee Singh Sup : *Dr. H. L. Agrawal*

The present thesis entitled, "SOME ASPECTS OF HEAT AND MASS TRANSFER IN MHD FLOWS" comprises the study of some problems on hydromagnetic free convection and mass transfer in rotating and non-rotating viscous incompressible, electrically conducting fluid in the presence of strong transverse magnetic field.

The thesis consists of six chapters. In the first chapter the basic concepts required in the development of the MHD theory have been discussed along with a review of the work done by the previous workers in this field, and their relations to the present work have also been shown.

In Chapter II, an analysis of Hall current on the combined effects of thermal and mass diffusion of an electrically conducting liquid past an infinite vertical porous plate is performed. Analytical expressions for the velocity and temperature fields are derived. The effects of various parameters on the velocity and temperature are shown graphically and in tabular form.

In Chapter III, an investigation is made to analyse the effects of Hall currents and viscous dissipation on hydromagnetic free convective flow in the Ekman layer of a conducting liquid past an infinite porous plate. The problem is solved analytically. The velocity and temperature profiles are shown on graphs and the numerical values of rate of heat transfer and skin-friction at the plate in x and y directions have been tabulated.

In Chapter IV, an analysis of Hall current on MHD natural convective flow past an infinite vertical porous plate in a rotating frame of

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reference have been carried out when the free stream oscillates about a constant non-zero mean. Approximate solutions to the coupled, non-linear equations governing the flow field are derived. The effects of different parameters on velocity and temperature distribution are shown graphically and numerically.

In Chapter V, Hall effect on the hydromagnetic free convection resulting from the combined effects of thermal and mass diffusion of an electrically conducting liquid past an infinite vertical porous plate in a rotating system have been analysed. The expressions for the velocity and temperature in boundary layer and the skin-friction and the rate of heat transfer on the plate are derived. The effects of different parameters on the flow fields are discussed with the help of graphs and tables.

Chapter VI deals with the study of combined effects of Hall current and plate temperature oscillation on the hydromagnetic free convective flow past a vertical infinite porous plate in rotating and non-rotating fluids. The expressions for the velocity and temperature fields are derived. The effects of various parameters on the velocity and on shear stress are shown by graphs and tables.

These investigations have been carried out by me under these inspiring guidance of Dr. H. L. Agrawal, Professor of Applied Mathematics, Institute of Technology, Banaras Hindu University, to whom I wish to record my sincere thanks for his valuable suggestions, keen interest and encouragement. To him I owe a deep debt of gratitude.

TRIPLE HYPERGEOMETRIC SERIES AND THE POLYNOMIAL SET $\{Z_{\gamma_1 n}(x, y)\}$

Nalin Kumar Tewari Sup : *Dr. R. N. Pandey*

The thesis entitled, "Triple Hypergeometric Series and the Polynomial Set $\{Z_{\gamma_1 n}(x, y)\}$" consists of five chapters with a bibliography followed by appendix.

Chapter I comprises mainly a historical account of different unification of polynomials such as Hermite polynomials, Laguerre polynomials, Bessel polynomials and generalizations associated with them by different authors. The unification of polynomials has been arrived at by considering different ways of defining them namely generating

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function, Rodrigues' formulae, Hypergeometric forms, Recurrence relations Differential equations, Difference equation etc. Considering these aspects, I have arranged different unifications by various authors under different headings. At the end of the chapter lemmas and notations which have been extensively used throughout the thesis, are collected together.

In Chapter II a generalized polynomial set $\{Z_{\gamma_1 n}(x, y)\}$ has been defined by means of a generating function. The study of these polynomials initiated in the present chapter is concerned with three main problems, namely, the identification of the set, explicit expressions of the polynomials and generating functions.

The generating function of the set contains triple hypergeometric series defined by Srivastava, H. M., which is a unification of Lauricella's fourteen hypergeometric functions. The polynomial set covers more than twenty-five orthogonal and non-orthogonal polynomials such as Hermite, Rice, Gattlieb, Legendre, Jackson polynomials etc. and discrete polynomials of Charlier, Meixner, Krawtchouk and Hahn.

These polynomials are of utmost importance for scientists and engineers, because these occur in the solutions of differential equations, integral equations, integro-differential equations, etc. which described physical problems. For example Hermite polynomials have their applications in various problems of quantum mechanical harmonic oscillator. Fourier series in orthogonal Jacobi polynomials of various negative powers of the distance between two moving bodies have found applications in arbitrary Kaplenirn ellipses. Discrete polynomials such as Charlier and Meixner have their applications in probability theory. Many orthogonal polynomials have their applications in quantum mechanics, chemical kinetics, electromagnetic theory, fluid mechanics, sub-surface hydrology conduction heat transfer, etc.

This shows that the unification of these polynomials mentioned above by the newly defined polynomial set $\{Z_{\gamma_1 n}(x, y)\}$ may be of great use in further development of the subject.

Later in the chapter hypergeometric forms of the polynomial set have been obtained and various particular cases have been deduced from these hypergeometric forms. Further, other hypergeometric forms for the set have been worked out and hypergeometric forms for a number of known polynomials have been deduced as particular cases.

Finally, a number of generating functions for some well known polynomials have been deduced from the generating function and a

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symmetric introduction to and several applications of a method of obtaining bilinear or bilateral relations for a large variety of sequences of special functions have been studied.

The object of the chapter III is to derive some properties of the polynomial set $\{Z_{\gamma_1 n}(x, y)\}$ from which various known and unknown results for classical polynomials have been deduced. Further $y^{\beta_1 n}$ has been expressed in a finite series of particularised polynomial set $\{Z_{\gamma_1 n}(x, y)\}$. Finally the chapter concludes with a set of four recurrence relations for the polynomial set $\{Z^{*}_{\gamma_1 n}(x, y)\}$, followed by particular cases. Some of the results obtained as particular cases are believed to be new.

Chapter IV deals with the study of ordinary and partial differential equations and Rodrigues' type formulae related to the polynomial set $\{Z^{*}_{\gamma_1 n}(x, y)\}$.

An attempt has been made to derive the ordinary differential equations with respect to x and y in terms of the operators $\theta_1 \left(\equiv x\frac{\partial}{\partial x}\right)$ and $\theta_2 \left(\equiv y\frac{\partial}{\partial y}\right)$. These differential equations have been given in the form of theorems. Other solution of the differential equations have also been worked out. In fact, it is first verified that the polynomial set satisfies foregoing differential equations and then an equation is actually solved giving rise to the result that the polynomial set $\{Z^{*}_{\gamma_1 n}(x, y)\}$ is one of the solutions of the differential equation and other solutions are functions.

It is interesting to note that the differential equations thus obtained will yield, as particular cases, a number of differential equations for known polynomials, when we put the values of the parameters given in Chapter II.

The derivation of the partial differential equations of the polynomial set in terms of the operator $\phi \left(= \frac{x}{\alpha_2}\frac{\partial}{\partial x}\right)$ and $\psi \left(\equiv \frac{v}{\beta_3}\frac{\partial}{\partial y}\right)$ have been obtained.

In the last section of this chapter the generalized polynomial set $\{Z^{*}_{\gamma_1 n}(x, y)\}$ has been expressed as the n-th derivatives of some hypergeometric polynomials. Some known and unknown results for classical polynomials have been worked out from the general result.

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Chapter V deals with the study of asymptotic behaviour, integral representations and integrals involving $Z^{*}_{\gamma_1 n}(x, y)$.

The symmetric study of the asymptotic behaviours has been done from the polynomial set when order tends to infinity. These results have been given in the form of theorems. For illustrations particular cases have also been given.

Further, a set of integrals representing the polynomial set $\{ Z^{*}_{\gamma_1 n}(x, y)\}$ have been obtained. In all, there are four types of representations :

(i) Finite single integral representation,
(ii) Infinite single integral representation,
(iii) Finite double integral representation, and
(iv) Infinite double integral representation.

Each type of integral representation is given in the form of theorems, also these theorems are followed by their deductions for different values of the parameters given in Chapter II. These deduction are useful for scientists and engineers. The main tool involved in arriving at these deductions are term by term integration.

Lastly we have evaluated an infinite integral involving product of H-functions of two variables and the generalized polynomials $Z^{*}_{\gamma_1 n}(x, y)$. The integral is of very general nature and contains as particular cases a number of interesting integrals involving well known special functions.

In Appendix, validity of the lemma given at the end of the introductory chapter has been shown.

CERTAIN INVESTIGATIONS IN THE SUMMABILITY OF FOURIER SERIES AND ITS ALLIED SERIES

Vagish Narain Tripathi Sup : *Dr. L. M. Tripathi*

The present dissertation is an outcome of the investigation of the author in the Summability Theory. It consists of eleven chapters.

In the first chapter, which is introductory, an attempt has been made to present a brief account of the existing results which form a background for the author's investigations into the problems dealt with in the subsequent chapters of the Thesis.

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In Chapter II, we [11] have generalised the result of Singh [10] by establishing the following theorem on $|\overline{N},p_n|$ summability factors of an infinite series :

Theorem. Let $\{p_n\}$, $n>0$, be a non-negative monotonic non-increasing sequence of constants such that its non-vanishing nth partial sum $R_n \to \infty$ as $n \to \infty$. Let

$$K_n = \frac{1}{\overline{R}_n} \sum_{\nu=1}^{n} R_\nu a_\nu$$

denote the $(\overline{N},p_n)$ mean of the sequence $\left\{\frac{1}{p_n} R_n a_n\right\}$. If

$$p_n \sum_{\nu=1}^{n} |K_\nu| = O(1) \ (\overline{N}, p_n)$$

and $\{\epsilon_n\}$ is a bounded sequence such that

$$\Sigma \frac{p_n |\epsilon_n|}{R_n} = O(1)$$

and

$$\Sigma \frac{|\Delta^2 \epsilon_n|}{p_n} = O(1),$$

then the seris $\Sigma a_n \epsilon_n$ is summable $|\overline{N},p_n|$.

In Chapter III, we [12] have established the following theorem on K^λ—summability of a Fourier series, which generalises the theorem of Kathal [4] :

Theorem. Let $\{p_n\}$ be a non-negative, monotonic non-increasing sequence o constants such that $\sum_{\nu=0}^{n} p_\nu = R_n \to \infty$ as $n \to \infty$. Let $\epsilon(t)$ and $\mu(t)$ be two positive functions of t such that $\epsilon(t)$, $\mu(t)$ and $\frac{t\epsilon(t)}{\mu(t)}$ increase monotonically with t and

$$\epsilon(n) \log n = O\ [(\mu R_n)], \text{ as } n \to \infty.$$

If

$$\int_0^t |\phi(u)| \, du = o\left[\frac{t\epsilon(1/t)}{\mu(R\tau)}\right]$$

as $t \to +O$, where

$$\phi(t) = f(x+t)+f(x-t)-2f(x),$$

then the Fourier series is summable $K^\lambda (\lambda > O)$ to the sum f(x) at the point $t = x$.

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In Chapter IV of the present thesis, we have defined, for the first time, almost Euler summability (E,q) of order $q>O$ and obtained a very nice result for almost Euler summability of a Fourier series, which generalises the theorem of Sharma, Dixit and Shukla [7] on almost Borel summability of Fourier series, by establishing the following :

Theorem. Let $\lambda(t)$ and $K(t)$ be two positive functions of t such that $\lambda(t)$, $K(t)$ and $\frac{t\lambda(t)}{K(t)}$ increase monotonically with t and let $\{p_n\}$ be a non-negative, monotonic non-increasing sequence of constants such that its non-vanishing n^{th} partial sum $R_n \to \infty$ as $n \to \infty$. If

$$\int_0^t |\phi(u)|\, du = o\left[\frac{\lambda(1/t)p\tau}{\{K(R\tau)\}^{\delta}}\right] \text{ as } t \to O+$$

and

$$\int_{1/(n+m)}^{1/(n+m)\delta} \frac{|\phi(u)|}{u}\, du = o(1), \text{ as } n \to \infty,$$

where $o<\delta<1$, uniformly with respect to m, then the Fourier series is almost summable (E,q), $q>O$, to the sum f(x) at the point $t=x$, provided that

$$\lambda(n)\, R_n = O\left[\{K(R_n)\}^{\delta}\right], \text{ as } n \to \infty.$$

In Chapter V, we [13] have aimed at generalising the theorem of Rao [6] by proving the following theorem on strong Perron summability [P,1] of the (C,1) mean of a Fourier series :

Theorem. Let $\{p_n\}$ be a sequence of non-negative numbers and let the series $p(x)=\sum_{n=1}^{\infty} p_n x^n$ converge for all x, $O<x<1$, and $p(x) \uparrow \infty$ as $x \uparrow 1$.

If

$$\int_0^t |\phi(u)|\, du = o\left[\frac{p(1-t)}{p'(1-t)}\right], \text{ as } t \downarrow O,$$

$$\int_t^{\pi} \frac{|\phi(u)|}{u}\, du = o\,[p(1-t)], \text{ as } t \downarrow O,$$

and

$$\sum_{n=1}^{\infty} n\, p_n\, y^n = O[p(y)], \text{ as } y \uparrow 1,$$

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then

$$\sum_{n=1}^{\infty} | \sigma_n(x)-f(x) | p_n y^n = o[p(y)], \text{ as } y \uparrow 1,$$

where $\sigma_n(x)$ is the (C,1) mean of the Fourier series.

In Chapter VI of the present thesis, we [14] have obtained the following result for $| C,\alpha |$ summability, $\alpha>1$, of a series associated with a Fourier series by extending the theorem of Hsiang (3) on $| C,1 |$ summability factors of a Fourier series at a given point.

Theorem 1. If

$$\int_t^{\pi} \frac{| \phi(u) |}{u} du = O\left[\{ \log^k (1/t) \}^{\eta} \right]$$

as $t \to +O$, where

$$\phi(t) = \tfrac{1}{2}\{f(x+t)+f(x-t)-2f(x)\},$$

then the series

$$\sum_{n=n_o}^{\infty} \frac{A_n(t)}{\prod_{\nu=1}^{k-1} (\log^{\nu} n)(\log^k n)^{1+\theta}}, \quad \theta>O,$$

is summable $| c,\alpha |$, $\alpha>1$, for $O<\eta<\theta$.

In order to prove the above theorem, we have first established the following theorem on $| c,\alpha |$ summability factors of an infinite series Σa_n.

Theorem 2. Let $\alpha>O$ and r be the least positive integer with $r \geqslant \alpha$. Let $\{\beta_n\}$ be a positive non-decreasing sequence and $\{\epsilon_n\}$ be such that $\epsilon_n \to O$ as $n \to \infty$ with $| \Delta \epsilon_n |$ non-increasing and satisfying

$$\sum_{n=1}^{\infty} n^r \beta_n | \Delta^{r+1} \epsilon_n | < \infty.$$

Then the series $\Sigma a_n \epsilon_n$ is summable $| c,\alpha |$, $\alpha>1$.

In Chapter VII, we [15] have extended the result of Mohanty and Nanda [5] by proving the following theorem on $(\bar{N}, p_n)$ summability of the derived series of a Fourier series.

Theorem. Let $\{p_n\}$ be a real, non-negative, monotonic non-increasing sequence of constants such that $\sum_{\nu=0}^{n} p_\nu = R_n \to \infty$ as $n \to \infty$ and

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$$\sum_{m=1}^{n-1} | \Delta m\, p_m | + n\, p_n = O(1), \text{ as } n \to \infty.$$

If $g(t) \in L(0, \pi)$ and

$$\int_t^{\pi} \frac{| g(u) |}{u} du = o\,(R_7), \text{ as } t \to o,$$

where

$$g(t) = \frac{\Psi\ (t)}{4 \sin \frac{t}{2}} - o,$$

with

$$\Psi\ (t) = f\,(x+t) - f\,(x-t)$$

and c being some function of x at $t = x$, then the derived series of the Fourier series is summable $(\overline{N}, p_n)$ to the sum c.

In Chapter VIII, our object is to improve and extend the theorem of Singh [9] by establishing the following theorem on $(J, p_m q_n)$ summbility of double Fourier series :

Theorem. Let $\{p_m\}$ and $\{q_n\}$ be two non-negative monotonic non-increasing sequences of constants decreasing steadily to zero such that $\{mp_m\}$ and $\{n\, q_n\}$ are bounded. If

$$\int_t^s \int_o^t \phi(u,v)\, du dv = o\,[sp(1-s)t\ q(1-t)]$$

and

$$\int_s^{\pi} \int_t^{\pi} \frac{\phi(u,v)}{u\ v} du\ dv = o\,[p(1-s)\ \ q(1-t)],$$

as $s \to +o$ and $t \to +o$, where

$$\phi(u, v) = f\,(x+u, y+v) + f\,(x+u, y-v)$$
$$+ f\,(x-u, y+v) + f\,(x-u, y-v) - 4f\,(x, y);$$

then the double Fourier series is summable (J, p_m, q_n) to $f(x, y)$.

In Chapter Ix of the present thesis, we [16] have generalised the theorem of Dwivedi [1] by obtaining the following result for uniform triangular matrix summability of Legendre series :

Theorem. Let us write

$$\Psi(t) = \Psi_{\theta}(t) = f\,\{\cos\,\theta - t)\} - f\,(\cos\theta)$$

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and let $o \leqslant t < \eta < \pi$ be fixed. If

$$\int_t^{\eta} \frac{|\Psi(u)|}{u^2} du = o\left[\frac{1}{t \log \frac{1}{t}}\right],$$

as $t \to +o$, uniformly in a set E defined in the interval $(-1, 1)$ in which $f(x)$ is bounded, then the Legendre series associated with the Lebesgue integrable function $f(x)$ in the range $(-1, 1)$ is summable $(\wedge)$ uniformly in E to the sum $f(x)$.

The study of the summability of Jacobi series by Nörlund method has been performed by several researchers. In the same line, Chapter X is devoted to the study of Nörlund summability of Jacobi series, where we have made an attempt to improve the theorem of Gupta under very general condition by establishing the following :

Theorem. Let $\{p_n\}$ be a non-negative, monotonic non-increasing sequence of constants such that its non-vanishing n^{th} partial sum $R_n \to \infty$ as $n \to \infty$ with

$$\log n = O(R_n),$$
$$n(2\alpha+1)/2 = o(R_n)$$

and

$$\sum_{k=2}^{n} \frac{R_k}{k(2\alpha+3)/2 \log k} = O\left[\frac{R_n}{n(2\alpha+1)/2}\right],$$

as $n \to \infty$; $\alpha > -\frac{1}{2}$, $\beta - \alpha > -1$, $\beta + \alpha \geqslant -1$.

Let $f(x)$ be defined in the closed interval $[-1, 1]$ such that the integral

$$\int_{-1}^{1} (1-x)^{\alpha} (1+x)^{\beta} f(x) dx$$

with $\alpha > -1$, $\beta > -1$ exists in the sense of Lebesgue. Let us write

$$F(\theta) = \{f(\cos\theta) - A\} (\sin \theta/2)^{2\alpha+1} (\cos \theta/2)^{2\beta+1},$$

where A is fixed and let $\tau = [1/t]$ denote the integral part of $1/t$. If

$$\int_o^t |F(\theta)| \, d\theta = o\left[\frac{t^{2\alpha+2}}{R_\tau}\right],$$

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as $t \to 0$ and the antipole condition

$$\int_{-1}^{b} (1+x)^{(\beta-\alpha-1)/2} \mid f(x) \mid dx < \infty ,$$

is satisfied, b being fixed, then the Jacobi series corresponding to the function f(x) is summable (N, p_n) to the sum A at the point $x=1$.

In the last chapter of the present thesis, we have established the following theorem on the degree of approximation to a function by triangular matrix of its derived Fourier series which is analogous to the result of Siddiqui for the degree of approximation to a function by Cesaro means of its Fourier series.

Theorem. Let t'_n denote the ($\wedge$) mean of the derived series of the Fourier series of a 2π—periodic and Lebesgue integrable function f(t) in the interval $(-\pi, \pi)$ and $\psi(t)$ be a positive increasing function such that

$$\int_{1/n}^{\delta} \frac{\psi(t)}{t^2} dt = O\,[n\,\psi\,(1/n)]$$

as $n \to \infty$. Let us write

$$g(t) = g_x(t) = f(x+t) - f(x-t) - 2t\,f'(x),$$

where f' (x) is the first derivative of f(t) at $t=x$. If

$$\int_{o}^{t} \mid dg(u) \mid = O\,[\psi(t)]$$

where $0 \leqslant t \leqslant \delta \leqslant \pi$, then

$$t'_n - f'(x) = O\,[\psi(1/n)]$$

as $n \to \infty$.

EVOLUTION OF NON-LINEAR WAVES UNDER HIGH TEMPERATURE CONDUCTIONS

Rama Pati Upadhyay Sup : *Dr. Rishi Ram Sharma*

The present thesis entitled "Evolution of Non-linear waves under High Temperature Conditions", comprises of five chapters. The first chapter is introductory and it provides a general review and historical background of developments in various aspects of non-linear waves. Several authors have contributed in the development of the shock wave

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theory in different directions and some of their significant contributions have been quoted in this chapter. Furthermore, this chapter provides the mathematical background and basic equations of different flow fields, which we shall need in the subsequent chapters.

The second chapter has been divided into two parts. In the first part we have studied the non-linear acoustic wave propagation in an optically thin medium of magneto-fluids. The time-dependence of wave amplitude has been discussed and the critical time t_c is determined when an acoustic wave of finite amplitude breaks at the cusp of intersecting characteristics and a shock-type discontinuity appears. The magnetic field effects and the radiative heat emission effects on the growth and decay of a non-linear acoustic wave have been studied.

In the second part the characteristic solutions of a week wave problem in gaseous flows at very high temperature has been obtained. The critical time t_c required for the breakdown of characteristic solutions has been determined. It is shown that all compressive waves will grow and terminate into shock waves, while all expansion waves will decay out.

The third chapter deals with the propagation of weak non-linear wave, headed by wave fronts of arbitrary shape moving into a non-uniform and inhomogeneous medium of a general class of relaxing fluids. The transport equations governing the rate of change of discontinuities in the normal derivatives of the flow variables are obtained and it is found that the non-linearity effects resulting in the steepening of wave fronts face resistance from relaxation effects. The growth and decay properties of weak non-linear waves along bicharacteristic curve haves been studied.

The fourth chapter has also been divided into two parts. In the first part the propagation of a weak MHD discontinuity has been studied by taking into account the effect of thermal conduction. The global behaviour of the wave amplitude a (ψ) has been investigated for both compressive and expansion waves. It is found that the thermal conduction has a destabilizing effect on the wave in the sense that it accelerates the process of shock formation. It is found that the critical time t_c decreases under the thermal conduction effect. The amplitude of a expansion wave ($\alpha > 0$) decreases monotonically and tends to zero, which shows that all expansion waves will ultimately decay out, whereas compressive waves will termihate into shock waves within a finite time. In the second part the effects of thermal radiation and conduction on the global behaviour of weak MHD

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discontinuities have been studied under a quasi-equilibrium and quasi-isotropic hypothesis of the differential approximation to the radiative heat transfer equation. It is found that the existence of the time-dependent radiation field gives rise to a radiation induced wave which has a negligibly small effect on the non-relativistic flow properties of the gasdynamic field. It is shown that the radiation stresses resist the steepening tendency of a compressive wave and help in stabilizing it, whereas the thermal conduction counter effect and has a tendency to destabilize it. It shows that under radiation effects the shock formation is either disallowed or delayed. The two cases of diverging waves and converging waves have been studied separately to answer particular question as when a shock discontinuity is formed or disallowed under curvature effects.

In the fifth chapter we have found self-similar solutions of isothermal flows behind a cylindrical magnetogasdynamic blast wave. A strong cylindrical shock wave generated by a sudden line source explosion in an inhomogeneous medium of electrically conducting gas has been studied. Numerical and analytical treatments have been presented and an uniformly valid distribution of pressure, density and velocity profiles have been determined and the magnetic field effects on the flow distributions have been investigated. The shock propagation law is determined by extending the Whitham's rule for an MHD flow in the finite electrical conductivity.

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PHYSICS

AN EXPERIMENTAL STUDY OF FRAGMENTATION PROCESS AND SOME GENERAL ASPECTS OF HIGH ENERGY NUCLEUS-NUCLEUS COLLISIONS

Ramranjan Bhanja Sup : *Dr. S. K. Tuli*

The study of heavy ion interactions in the field of high energy nuclear physics started with the discovery of heavy primary nuclei in cosmic radiation around 1948. For more than two decades this field made use of cosmic radiation as projectile and nuclear emulsions as detector. The limitations of precise beam energy detectors and the increasing demands of theory prompted the experimentalists to think over an alternate possible way of accelerating heavy ions to high energies in the laboratory. Successful surmounting of these problems gave rise to a new fascinating independent field called Relativistic Heavy Ion Physics (RHI) when the first heavy ion accelerator called Bevalac accelerated ions upto ^{20}Ne to energies of 2 GeV/nucleon in August 1971 at Berkeley. Since then many more discoveries have taken place in this area which have in turn lead to the building of more accelerators[1] having capability of accelerating heavier ions to higher energies and to the design and construction of sophisticated detectors[2].

Although no direct experimental evidence has been found yet for the existence of the expected exotic phenomena, other interesting concepts such as factorization, scaling or limiting fragmentation have been verified at energies of 1—2 GeV/A[3]. Several theoretical models for heavy ion interactions have been suggested[4]. Most of the models often predict two or three steps in the reaction scheme.

The present work is based on an experimental study of the interactions in nuclear emulsion induced by 2.1 GeV/A ^{14}N accelerated at the Berkeley Bevalac. The results are based on different types of measurements for multiplicity, angle, charge resolution and momentum distribution for around 1100 events collected by the line scanning method.

Main emphasis has been given to projectile fragmentation process with consideration to the variation in different target excitation regions as well as various reaction channels and targets in nuclear emulsions.

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The results have been compared to similar other experiments[5]) and the predictions of pertinent models[6]) in addition to the verification of limiting fragmentation and factorization characteristics. The typical Gaussian nature of the momentum distributions of multiply charged projectile fragments has been examined directly, from the estimation of momentum from the scattering measurements, and indirectly from their angular distributions. The $\sigma(p)$ thus obtained from the Gaussian distributions is employed to estimate the universally constant σ_0 (the recoil momentum carried away by the fragments) as well as the limiting temperature (excitation energy) characteristics. The emission angle distributions of helium projectile fragments are discussed in terms of predictions from moving relativistic Boltzmann distributions to obtain the value of excitation energy of the thermal source.

In addition to his some general characteristics from the point of view of multiparticle production in nucleus-nucleus collisions observed in this investigation, primarily concerning the angles and multiplicity parameters together with a comparison with the situation in hadron-nucleus collision are discussed. The KNO scaling in multiplicity distribution is investigated at such relatively low energy with a comparison to that of the hadron-hadron and hadron-nucleus collisions at high energy. Over and above, an event by event target differentiation in nuclear emulsion is attempted which thus lead to the study of collision mechanism with different targets.

Briefly speaking the thesis starts with an introduction to the general description of nucleus-nucleus collisions in addition to the information about the accelerators as well as detectors and then goes to the general theoretical background of AA collisions at high energy emphasising mainly the models pertinent to fragmentation processes with a brief description of related models. After the details of the experimental methods adopted in this experiment it then passes to the analysis of general characteristics of AA collisions observed in this study mostly in the form of presentation of angles (pseudo-rapidity) and multiplicities (multiplicity distributions, correlations and the KNO scaling) followed by the event by event target identification.

After a brief discussion of general characteristics, the analysis of fragmentation process has been started with the charge identification, as well as emission properties of multiply charged projectile fragments. The question of correlation to the target break up in various He nuclei reaction channels and in collisions with different targets leads to the verification of factorization concepts. Obviously this created interest

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in testing the limiting fragmentation hypothesis for relativistic projectile fragments in particular the Gaussian character of the momentum distributions directly from the scattering and indirectly from the projected angle distributions. Then we examine the limiting temperature concepts and analyse the space angle distributions.

A summary and a general overview of the work with important results and a discussion thereof is given in the concluding chapter. Some of the important conclusions in brief are :

(i) The validity of KNO scaling for multiplicity distribution of all the produced hadrons from relatively low energy ($\sim$2 GeV/A) to very high energy ($\sim$1000 GeV/A) is puzzling as the central assumption on which KNO scaling was based is not fulfilled in the energy region considered here. Thus we believe the apparent success of KNO scaling may be viewed as an empirical fact or stabilization of certain factors in the production mechanism.

(ii) The independence of emission angles and other properties of projectile He fragments irrespective of various channels and targets shows that the helium cross sections can be reasonably factorized into two parts in peripheral collision processes. One describing the breakup of the projectile independent of the target disintegration and the other showing the target breakup independent of the process in the projectile.

(iii) The agreement of projected angular distributions for $Z=2$ to $Z=5$ fragments emitted from $N_h \leqslant 8$ type events in emulsion with the single particle inclusive experiments thus leads to the conclusion that momentum distribution of the fragments that are selected only on the basis of their high rapidity without the knowledge of any target excitation and the fragments in the presence of high rapidity but with the knowledge of target excitation ($N_h \leqslant 8$) have no difference. This observation is consistent with the characteristics of limiting fragmentation hypothesis.

(iv) Our momentum distributions and its analysis for $\sigma(p)$ of projectile He fragments are consistent with observations of the validity of limiting fragmentation hypothesis around 2 GeV/A beam energy for fragment momenta up to$\sim$0.5 GeV/c in the projectile frame.

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STRUCTURAL AND ELECTRONIC CHARACTERISTICS OF TIN DICHALCOGENIDE CRYSTALS

Santa Chawla Sup : *Dr. O. N. Srivastava*

The layered semiconductors with their characteristic structural feature—polytypism, offer the potential possibility of obtaining a new class of materials. Here same chemical compound can exist in a number of distinctly different crystallographic phases corresponding to different electronic materials. Furthermore, many important electronic properties of semiconductors depend crucially upon the presence and distribution of defect levels within their forbidden gap. Therefore the measurements of the electronic properties and their correlation with the structural characteristics such as polytypism and the defect level distribution, will be very advantageous since materials with desired electronic properties can be obtained. Although there has been a surfeit of studies in regard to the investigations on the growth and structural characteristics of layered materials, comparatively sparse studies embodying the investigations on the electronic properties and their correlation with the structure have been done so far. Keeping this aspect in view, semiconducting layered crystals of tin dichalcogenides have been chosen in the present study for the exploration of the occurrence of polytypism and the correlation of the electronic properties with the structural characteristics.

In the present investigation detailed studies of the structure sensitive as well as defect sensitive electronic properties of tin dichalcogenides SnS_2, $SnSe_2$ and the solid solution system SnS_xSe_{2-x} have been carried out.

The single crystals of the tin dichalcogenides have been grown by iodine vapour transport technique in a horizontal two zone gradient furnace. The crystallographic characterisations of the as grown crystals have been carried out by X-ray diffraction oscillation technique. Both SnS_2 and $SnSe_2$ crystals are found to exhibit polytypism profusely. Several new polytypes have been encountered for SnS_2, in addition to those reported earlier. As far as SnS_2 is concerned, the occurrence of polytypism embodying a series of hexagonal and rhombohedral structures has been established for the first time in the present study.

Since polytypes correspond to distinct crystallographic phases, the structure dependent electronic parameters must also differ in a significant way. The most structure sensitive electronic parameter for a semi-

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conductor-visibly the band gap has been measured for different polytypes of SnS_2 and $SnSe_2$ from the variation of dark conductivity along the c-axis with temperature in the intrinsic conduction region. The results reveal that band gap varies markedly with polytype periodicity-for hexagonal polytypes the band gap decreases as the polytype periodicity increases starting from 2.18 eV for 2H-SnS_2 to 0.81 eV for 5OH-Sns_2 and 1.14 eV for 2H-$SnSe_2$ to 0.66 eV for 22H-$SnSe_2$; the band gap for the most common rhombohedral polytype (18R) of SnS_2 is 3.38 eV and higher period rhombohedral polytypes follow the same trend of decreasing band gap as the hexagonal polytypes do. The present investigation thus leads to a very significant result—the different polytypes of of SnS_2 and $SnSe_2$ correspond to effectively different electronic materials. The variation of band gap with polytype periodicity becomes intelligible in terms of a one dimensional band structure calculation based on the superlattice like configuration of different polytypes.

In order to explore the defect level distribution within the forbidden gap as well as to estimate the band gap of the solid solution system SnS_xSe_{2-x}, optical obsorption spectra have been taken in the infrared and visible region respectively. The results show that the optical band gap varies with the composition x in the series SnS_xSe_{2-x} starting from 2.25 eV for SnS_2 to 1.10 eV for $SnSe_2$. This observed variation is in conformity with the experimental results of Lee et al (Lee, P. A., Said, G., Davis, R. and Lim, T. H., 1969, J. Phys. Chem. Solids, *30*, 2719) and the theoretical band structure calculations (Aymerich, F., Meloni, F. and Mula, G., 1973, Sol. St. commun., *12*, 139). Infrared transmission spectra in the 400 to 4000 cm^{-1} wavenumber range exhibits the presence of several minima indicating enhanced absorption for the promotion of electrons from the localised defect levels to the conduction band. The as grown SnS_2 crystals exhibit the presence of only three shallow donor levels at 0.053, 0.067 and 0.074 eV, whereas the crystals in the series SnS_xSe_{2-x} show several shallow as well as deep levels in the composition range $0.7 \leqslant x \leqslant 1.7$.

In order to find out the role of defect centres in the current transport process of the tin dichalcogenides, current voltage characteristics have been measured. The observations have revealed very interesting electronic effect namely the occurrence of the injection currents accompanied with current controlled negative resistance and switching in the as grown single crystals of SnS_xSe_{2-x} and doped crystals of SnS_2 respectively. The observed current-voltage characteristic typically comprises of an Ohm's Law ($I \propto V$) region followed by a space charge square law ($I \propto V^{1.5 \text{ to } 2}$) region which is connected to a high current-low voltage

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square law ($I \propto V^{1.5}$ to ^{2}) region through a negative resistance region where current increases very rapidly with the voltage decreasing to a lower value. The observed characteristic is typical to that of double injection with trapping and can be explained with the help of such a model. This observation clearly brings out the role of deep lying defect centres (levels) in the occurrence of negative resistance in tin dichalcogenides.

The as grown single crystals of SnS_2 show a very curious effect—the presence of a built-in voltage of considerable magnitude that differs from polytype to polytype. The effects of temperature and light illumination on the built-in voltage show quenching behaviour which gives evidence for trapping levels operating in the process. The observed features can be explained with the help of a model of non uniform distribution of carriers distributed in different trap levels.

STUDIES ON N_2-LASER AND GAS-PHASE PHOTOACOUSTICS WITH Ar+ LASER

Chhedi Lal Sup : *Dr. S. N. Thakur*

Laser radiation can be an extremely intense, sharply focusable and virtually single frequency electromagnetic radiation. Its interaction with matter gives rise to phenomena which had never been observed with electromagnetic radiation from conventional sources. It can be used to detect trace impurities, to trigger chemical reactions and to explore molecular structure. The advent of lasers has given rise to many new experimental spectroscopic techniques and has revived many old ones. The present work is concerned with the studies on the lasing characteristics of home made N_2- lasers and the use of laser radiations from an Ar+ laser for experiments in photoacoustics. In the first part of the thesis we describe the results of our studies on the beam qualities of transversely excited N_2- lasers employing different electrode configurations and intensity distribution in the rotational lines observed at different gas pressures. The principle of photoacoustics and some gas phase measurements using I_2 vapour and NO_2 gas form the content of the second part of the thesis. The whole thesis has been divided into six chapters.

The first chapter deals with the theoretical aspects of amplified spontaneous emission and the characteristics of laser emission. The mechanism of population inversion and the temporal characteristics of

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emission at 337.1 nm in N_2 has been discussed in the light of known spectroscopic and electron impact data on this molecule.

The details of fabrication of transversely as well as axially excited N_2- lasers have been discussed in the second chapter. The preionized low pressure TE-N_2- laser has a peak power in excess of 500 kW with a pulse duration of 7 ns and has pulse to pulse reproducibility of better than 99%. The axially excited N_2- laser has a peak power of 10 kW with a pulse duration of 20 ns. The variation of laser power out put as a function of excitation voltage and gas pressure in the laser channel have been measured and interpreted in terms of the existing theory.

Results of our studies on the spectral characteristics of N_2- laser radiation have been presented in third chapter. The relative intensities of the rotational lines have been determined from the high resolution spectra recorded on a 10.6 m concave grating spectrograph. The lines exhibit broadening on increasing the pressure of N_2- gas in the laser channel but the lines remain sharp when Argon gas is added to increase the total pressure of the gas mixture to the same level but keeping low partial pressure of N_2 gas. These observations have been interpreted in terms of an exchange of excitation energy between two N_2- molecules in the case of pure N_2- and in terms of collisional de-excitation in the presence of Argon. A comparative study of the relative intensities of transversely and longitudinally excited N_2- lasers with pressures of 25 torr and 4 torr respectively shows that fast rotational relaxation occurs in the former and slow rotational relaxation takes place in the latter.

Chapter four contains the measurements of beam profile of radiation from transversely as well as axially excited N_2- lasers. In the case of TE-N_2-laser radiation an asymmetry with peak intensity shifted toward the anode is observed. This asymmetry has beed explained in terms of propagation of ionization wavefront between the two electrodes. The dependence of this asymmetry on the gas pressure and on the electrode shape has been discussed in terms of a simple theoretical model. In the case of longitudinally excited N_2- laser discharge in the laser channel is initiated by dumping the electrical energy by sparking at one end of the laser channel. The intensity of the laser beam coming out of the channel end at which sparking takes place is found to be different from that at the other end and it has been explained in terms of ionization wavefront propagation in the interelectrode gap.

Chapter Five deals with the theory of generating photoacoustic signal in gaseous samples. It also contains discussions on the necessity of enhancing signals and the means to do so by design of acoustically

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resonant sample cells. The variation of photoacoustic signal (PAS) at different points along the length of a longitudinally resonant cell has been described in terms of a simple theoretical model. The dependence of photoacoustic signal on the density of absorbing species in a mixture of two or more gases has also been included. The theory of electret microphones, which are used as detectors in this technique, is also described briefly.

The design and performance of longitudinally resonant and Helmholtz resonant cells form the subject matter of chapter six. The magnitude of the photoacoustic signal is found to depend critically on the location of the microphone in a longitudinally resonant cell being largest at the antinode and smallest at the node of the standing wave pattern formed in the cell. The gas sample used in these experiments was Iodine vapour at room temperature (partial pressure 300 m torr) in the presence of air at atmospheric pressure. NO_2 has absorption in the blue-green portion of the visible spectrum and it was chosen for studying the variation of the photoacoustic signal as a function of partial pressure of the absorbing gas in air with total pressure of 1 atm. It has been found that the magnitude of the signal is not quite proportional to the square of density of the gas as demanded by theory.

A DESCRIPTION OF NUCLEAR TWO BODY RESONANT STATE IN POTENTIAL SCATTERING THEORY USING ANALYTICITY

V. J. Menon Sup : *Dr. A. V. Lagu*

The concept of a resonance occurs very widely in elastic, inelastic, stripping and rearrangement reactions. Although the phenomenological features of resonant processes along with the properties of transition amplitudes containing resonance poles are well understood and widely used (e.g. D. Robson, in Nuclear Spectroscopy and Reactions Part D, P. 179, ed. J. Cerny, Academic Press, 1975), yet a completely satisfactory prescription for the resonance wave function is not apparently available despite half a century of work. The need for such a wave function is crucial in certain areas of application e.g. in a stripping to unbound state calculation through the distorted wave Born approximation where mere knowledge of the T—matrix is not adequate (B. J. Cole, R. Huby and J. R. Mines, Phys. Lett. *33B*, 320, 1970; C. M. Vincent and H. T. Fortune, Phys. Rev. *C2*, 782, 1970; W. R. Coker and G. W.

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Hoffmann, Z. Physik *263*, 179, 1973; S. N. Mukherjee *et al*, Phys. Rev. *C15*, 1238, 1977). The main drawback of the existing models of the resonance state is that these models (e.g. S. Weinberg, Phys. Rev, *131*, 440, 1963; F. Coester and L. Schlessinger, Ann. Phys. (N. Y.) *78*, 90, 1973; L. Fonda, G. C. Ghiradi and A. Rimini, Rep. Prog. Phys. *41*, 587, 1978; T. Berggren, Nucl. Phys. *389*, 261 1982) do not satisfy the twin requirements of correct analytic properties in the momentum plane together with desirable quantum mechanical constraints. The central aim of the present thesis is, therefore, to construct a satisfactory state vector for a two body resonance formed through real (Hermitian) short range potentials using the twin requirements just referred to.

Among the several descriptions of the resonance state in the available literature two different types of theories are worth mentioning here. In the first type of the so called *eigenstate* theories the unstable particle wave function is an eigenfunction of the Hamiltonian H belonging to a complex energy eigenvalue, and it is regular or irregular at the origin depending upon whether it is a Gamow (e. g. A. J. F. Siegert, Phys. Rev. *56*, 750, 1939) or a Kim-Vasavada (Y.S. Kim and K.V. Vasavadev, Phys. Rev. *D5*, 1002, 1972) state. The main drawback of the eigenstate theories is that the involved state becomes non-normalizable due to the blowing up of the probability density either at infinity or at the origin. In the second type of the so called *wave packet* theories (e.g. L. Fonda *et al*) the quasi-stationary state is expanded in terms of the continuum eigenstates of the Hamiltonian H with energy-dependent coefficients. Those authors who have used this approach to the resonance state earlier were primarily interested in studying possible deviations from the exponential decay law (e. g. L. A. Khalfin, Soviet Physics (JETP) *6*, 1053, 1958), and only in one isolated case the wave packet was used in a deuteron stripping calculation (L. Schlessinger and G. L. Payne, Phys. Rev. *C6*, 2047, 1972). Consequently, these workers did not focus attention on pinpointing the precise algebraic form and properties of the expansion coefficients and, indeed, their resulting states have large ambiguities. It is obvious that in order to make the wave packet description acquire a sound theoretical footing and thereby to become useful in applications the expansion coefficients must be determined as uniquely as possible, a task which we have tried to accomplish in this thesis by employing the analytic properties of potential scattering theory as a powerful tool.

For the sake of ready reference we begin Chapter I by summarizing our notation, the assumptions on the two body potential, relevant formulae from standard scattering theory (R.G. Newton, Scattering Theory

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of Waves and Particles, Ch. 12, McGraw Hill, N. Y., 1966), and finally some new mathematical results derived by us. In particular, analytic properties in the complex momentum plane have been listed for the class of local potential V (r) which vanish identically outside a finite range as well as nonlocal potentials V (p, q) which are rational separable functions of momenta. Also the new propositions established are concerning e. g. the eigenfunction expansion of irregular solutions, and the pole structure of a class of integral representations.

In Second Chapter which also serves as the Introduction to the subject matter of the thesis, we present a critical survey of the various aspects of the phenomenology of resonances and their wave function. In particular, the eigenstate and wave packet theories, briefly referred to in the second paragraph above, have been discussed in detail along with other available approaches and the known properties of the Briet-Wigner amplitude are recapitulated. The review of the time development aspects has, however, been done at the beginning of Chapter V for reasons of cohesion.

The Third Chapter which may be regarded as original, contains the details of our own construction of the unstable state at time $t=0$. Given a pole of the T—matrix in a wave of orbital angular momentum l at complex momentum k_j (i.e., at complex energy $E_j=W-i\Gamma/2$) we set up the following wave packet to represent the jth resonance :

$$|\xi_j\rangle=(2n^2)^{-1}\int_0^\infty dk\, k^2\, |\Psi^-_k\rangle\, \rho^+_j(k)$$

where $|\Psi^-_k\rangle$ referes to the incoming type scattering state and $\rho^+_j(k)$ is the unknown expansion coefficient for which we write down a rather general form consistent with analyticity. A novel feature of the model is that the evaluation of various related quantities such as the packet vertex function, the radial wave function, etc. can be carried out in closed form with the help of Cauchy's theorem. We show e. g. that if V(r) is sharp cut-of then the radial wave function $\xi_j(r)$ is regular like r^l as $r\to o$ and is asymptotically damped like $1/r^{l+1}(l=1,2)$ which properties were not proved by any of the earlier authors (vide Fonda *et al*).

In Chapter Four, which is also original, we come to the question of fixing an adjustable function Z(k) appearing in ρ. For this purpose the following three plausibility conditions are imposed : (i) given a free momentum p the packet vertex function $\langle p\,|\,V\,|\,\xi_j\rangle$ equals the exact vertex function of the underlying Gamow state (ii) the matrix

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elements $<\xi_j \mid H^m \mid \xi_j>$ are finite where m=0,1 refers respectively, to the norm, average energy; and (iii) the resonance-saturated half-shell amplitude $<p \mid VI_j \mid \Psi_k^+>$ has the correct pole residues at $k=k_j;-k_j^+$ where I_j is a resonance-saturation operator. We prove that these quantum conditions are satisfied approximately for narrow widths if I_j is set up in the one dimensional scheme (i. e., when $|\xi_j>$ equals its own time-reversed state $|\overset{\sim}{\xi}_j>$), but satisfied exactly for arbitrary widths if I_j is constructed in the two dimensional philosophy (i.e., when $|\xi_j>$ and $|\overset{\sim}{\xi}_j>$ are linearly independent). The formula for ρ which emerges ultimately is

$$\rho_j^+(k) = \frac{D^-(k)\, Z(k)}{(k^2-k_j^2)\,(k^2-k_j^{+2})}$$

where $D^-(k)$ is the conjugate Fredholm denominator and Z (k) is an analytically known function. Two remarkable features of the theory at this stage are (1) the conditions (i) and (iii) above are novel, i.e., used by us for the first time, and (2) the roles of the resonance and capture poles have become unambiguous. Next, we identify the resonant and background contributions to the amplitude and make a comparison with the Breit-Wigner prescription. Finally, the construction procedure for ρ is explicitly demonstrated for three soluble models viz. the square well, Yamaguchi, and delta-shell interactions.

Fifth Chapter begins with a review of the previous work done on the time-dependent nondecay probability of an unstable system either in isolation or in interaction with the environ ment, and we show how this probability can be computed also in our model. Next, we consider the important question of evaluating the wave function $\xi_j(r, t) = <r\, e^{-iHt} \mid \xi_j>$ at large r for positive times (this question has been mostly ignored by earlier authors). By giving due consideration to the analytic structure of the integrand, and by doing careful contour deformations it is demonstrated that the probability flux is expressible in New simple algebraic form, the requirement of 'casuality' holds, and the exponential law is valid for about n' life times where $n' \sim O(\text{long } \frac{W}{\Gamma})$. Such an estimate of n' has not been given earlier in the context of flux. The physical role of the 'capture' pole and meaning of the 'bare' state are also clarified.

Although the primary emphasis of the thesis has been on formalism, we describe in Chapter VI two simple applications of the present

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model in order to demonstrate its viability. In the first application (which is a test calculation) we numerically compare, for the Yamaguchi potential, the elastic scattering cross section obtained by our saturation scheme against the exact as well as the Breit-Wigner formulae. In the second (which is a practical application) we carry out a stripping to unbound state calculation of the type A (d, p) C, where A is a spin zero nucleus and C is the residual nucleus in a specific resonant state. The DWBA matrix element for the process is known to contain $|\chi_n>$, the neutron wave function in C, for which one of the possible artifacts is to use the n—A scattering stated damped by a Gaussian factor (e.g. S.N. Mukherjee *et al*, Phys. Rev. *C15* 1238, 1977). We, however, suggest that $|\chi_n> = \sqrt{(\Gamma^e/\Gamma)}\ |\xi_j>$ where Γ^e is the experimental width, $|\xi_j>$ our wave packet in the one-dimensional scheme, and Γ the single-particle width is an assumed potential well. Because the realistic Woods-Saxon potential V_{nA} is not soluble we replace it by a square well of suitable range and depth. This replacement is physically justified for low energy resonances because then the shape-dependence of the interaction should not be crucial, and further-more a definite mathematical advantage is gained in the sense that the wave function $\chi_n(r)$ is now known analytically. We compare numerically the predicted outgoing proton angular distribution $\sigma_p(\theta)$ against the same resulting from other prescriptions for $|\chi_n>$. The experimental data (S. E. Darden *et al*. Nucl. Phys. *A208*, 77 1973) are taken for two different nuclei viz. excitation of the 5.083 MeV level of ^{17}O and the 6.864 MeV level of ^{18}C at 13.3 and 15.0 MeV incident deuteron energies, respectively. Both the shape and absolute normalization of our $\sigma_p(\theta)$ are satisfactory for ^{17}O, and rather dramatic in the case of ^{18}C. This feature is in contrast to the predictions of the Gaussian damping method where the shape of $\sigma_p(\theta)$ worsens and the normalization has to be adjusted through a spectroscopic factor.

The main conclusions of our work and remarks about its further prospects appear in Chapter VII. In particular, the following points are worth emphasizing : (i) a mathematical offshoot of our investigations has been the establishment of some new propositions in scattering theory; (ii) the wave packet philosophy, in general, is ideally suited to describe a normalizable resonance state, and the novel constraints imposed by us along with analyticity do fix the $\rho^+_j(k)$ satisfactorily. The firel form of ρ is so appealing that it should work even for potentials with a tail provided the effect of the cut in the k-plane is small composed to that of the poles at k_j; $-k^+_j$; (iii) the

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setting up of our saturation schemes, the property that ξ_j (r) falls off at infinity as an inverse power, and the fact that the exponejtial law for flux should hold for about n' lifetimes are also new; (iv) our stripping to unbound state calculation gives good results both for the shape and absolute normalization of the proton angular distribution. The fact that this happens even when the neutron-nucleus potential is replaced by a spin-independent square well may be attributed to the inherent merits of our approach, and we areo ptimistic that a more comprehensive calculation employing an Woods-Saxon potential with spin-orbit coupling will give improved fits not only to $\sigma_p(\theta)$ but also to the polarization data; (V) further areas where our model with appropriate refinements may have bright applicational prospects are calculations relating to resonance components of bound states (R. D. Amado, Phys. Rev. *C10*, 1095, 1979), production of unstable states by cluster-transfer in heavy ion reactions (K. Nagatani *et al*, Phys. Rev. Lett *43*, 1480, 1979), dynamics of resonances in particle physics (M. Rcos *et al*, Review of Particle Properties, CERN, 1982), excitation of metastables in atomic/molecular processes (G. Schulz, Rev. Mod Phys. *45*, 378 and 423, 1973), etc.

SOME STUDIES ON HEAVY-ION COLLISIONS

L. N. Pandey Sup : *Dr. S. N. Mukharjee*

In the recent years, the heavy-ion physics has played a significant role in relaxing the limitations that have been imposed on the study of nuclear physics. Limitations are nuclear charge and mass number, spherical shape, normal temperature and pressure, and reaction mechanism. The influence of very heavy-ion accelerator is already being felt in theoretical chemistry, in atomic physics, and in quantum electrodynamics as well as in nuclear physics itself.

The present thesis concerns with the theoretical investigations of some heavy ion collisions over a wide range of projectile incident energy and nuclear charge and mass numbers. One is quite tempted to use semiclassical concepts in order to describe the collisions of two heavy-ions at medium and intermediate energies. The large incident energy and the large masses involved bring many quanta into the system and thus render semiclassical description valid. The main interest of using a semiclassical approach is to find out what optical system nuclei build

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up, knowing the object (incident flux at infinity) and the image (measured cross section). In the above approach one should be able to follow the classical trajectories in order to understand physics of the heavy-ion reactions.

After giving in Chapter 1, a general introduction of the subject of heavy-ion collisions in the context of the present investigation, we make a critical examination of 'diffraction model' of heavy-ion collisions for incident projectile energy around the Coulomb barrier. The Chapters II and III essentially contain the diffraction theory and its applications.

The elastic scattering of heavy-ions, ^{20}Ne on ^{208}Pb; ^{20}Ne on ^{235}U; ^{84}Kr on ^{208}Pb and ^{84}Kr on ^{232}Th, are examined within the framework of Frahn's diffraction model. An analysis of the experiment using the 'quarter point recipe' of the expected Fresnel cross-sections yields a larger radius for ^{208}Pb than the radii for ^{235}U and ^{232}Th. It is shown that the inclusion of the nuclear deformation in the model removes the above anomaly in the radii and the assumption of smooth cutoff of the angular momentum simultaneously leads to a better fit to elastic scattering data, compared to those obtained by the earlier workers on the assumption of sharp cutoff. The target radius, obtained through quarter point analysis, shows dependence on the incident projectile energy.

Similar radius anomaly is also observed in the analysis of collisions of ^{16}O on ^{24}Mg and ^{28}Si targets around incindent energy of 72 MeV. It is found that the introduction of quadrupole deformation cannot resolve the above anomaly and the inclusion of higher order deformation is called for.

By analysing a substantial amount of data on elastic collision of deformed heavy-ions we hope to have shown that Frahn's diffraction model, when includes nuclear deformation and the concept of angular momentum space window, can provide a valid description of elastic heavy-ion collisions. One should also examine whether the physical interpretation of heavy-ion scattering entailed by the diffraction model is at par with optical model calculations.

The question of nuclear dissipation is discussed in Chapter IV in context of heavy-ion fission instead of deep-inelastic collision, which has been extensively studied by earlier workers.

Energy dissipation during heavy-ion nuclear fission has been calculated by employing one dimensional time dependent frictional Schrodinger equation. The variation of loss of energy with respect to

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the shape of the fissioning system follows the same trend as the classical frictional matrix. The dissipative loss of kinetic energy with respect to time is also shown.

Further analysis is necessary as concerns the role of nuclear friction for heavy-ion fission. The theory should be extended to three dimension in order to include simultaneously, the Coulomb, nuclear and centrifugal forces, however, on the expense of computer time. Our preliminary calculations here already showed that the classical form of friction tensor can be well incorporated in the quantal description of heavy-ion fission.

Finally, we enter a new era in nuclear physics i.e. high energy (relativistic) heavy-ion collision. Particularly the role of thermodynamic model (Fireball model) in the analysis of some recent experimental data are discussed in Chapter V.

The fireball model predictions of proton inclusive spectra obtained in the collision of Ar on Ar, K and Pb targets at 800 MeV/nucleon projectile energy, indicate that no single value of critical density can fit a particular type of collision data at all angles and energies. Present analysis requires a greater value of critical density than that usually used.

There is no reason for us to restrict the final products to protons and neutrons only. The fireball model can be used to explain the production of composites (d,t,He, etc.) and particles (pions, kaons, etc.). The inclusion of the deltas has a strong influence on the slope of the pion inclusive cross sections; the influence is significant even on the proton inclusive spectrum. Inclusion of pions and deltas cools the fireball; inclusion of the composite leads to an increase in the temperature. Therefore, the role of critical density in the fireball model predictions should be examined in each cases.

The last Chapter VI gives a brief account of the role of deuteron breakup in the field of a heavy target. Though this is not directly related to the main theme of the thesis yet it is included as a supplement, in accordance with the rule 24(b) of Ph. D. Ordinance, which permits a candidate to present his work which he has done in any other field for the advancement of learning.

The effect of deuteron breakup channel on the elastic scattering of deuteron on lead target around 80 MeV ineident deuteron energy has been examined. It is found that the large difference between experimental values and folding model predictions could mostly be explained in terms of deuteron breakup effects.

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SPECTROSCOPIC STUDIES OF DIATOMIC MERCURY HALIDES

Awadhesh Kumar Rai Sup : *Dr. D. K. Rai*

The present work is devoted to the elucidation of the electronic spectrum of diatomic mercury halides. These molecules have been selected for study mainly for two reasons. Firstly for the past several years, our laboratory has been engaged in the study of the electronic sperctra of heavy diatomic and mercury compounds were so far not investigated. Secondly and more importantly, recent success in the observation of Laser action in electron beam excited mixtures of Xe, Ar, Hg and hydrogen halides, wherein the lasing transition was identified as a bound-bound transition of diatomic halides of mercury, has emphasized the necessity of having reliable spectroscopic data on these molecules. Review of the earlier work on these spectra revealed many discrepancies in the available data and ambiguities, not to speak of many gaps in our knowledge about these spectra.

The work described in the present thesis has helped in clarifying some of the assignments given earlier and has resulted in more reliable molecular parameters for most of the known electronic states of these molecules. The thesis is divided in six Chapters. The first chapter gives a brief summary of the relevant theory.

The experimental details are given in Chapter 2. Spectra of diatomic mercury halides were photographed using natural HgX_2 (X—Cl, Br, I) of 99.9% purity in a transformer discharge through the flowing vapour. A π type discharge tube approximately 25 cm in length and 4 mm internal diameter with Ni electrodes was used and 6-10 mA current at 2.5 kV was found suitable for the proper excitation of the bands. During the exposure a mild heating of the sample to maintain proper vapour pressure in the discharge tube was found necessary. Exposures upto eight hours for the D—X system of HgCl, and thirty hours for the C—X and the D—X systems of HgBr and the C—X, the DX and the E_1—X systems of HgI were needed to record the spectra in the third order of a 10.6 m concave grating spectrograph (0.22 Å/mm reciprocal dispersion and $\simeq$ 500000 resolution) on 400 ASA panchromatic films. A Corning Glass UG—11 filter was used to cut off the unwanted second order radiation in the case of HgBr and HgI. The bands of the C—X system of HgCl, the E—X system of HgBr and the E_2—X system of HgI could not be photographed on the 10.6 m concave grating and we have used plates taken on a 6.6 m grating spectrograph in the second order.

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The bands of the E—X system of HgBr were recorded on a two prism quartz Steinheil spectrograph. The rotation structure has been measured using a comparator with a least count of 10^{-4} mm. Our measurements are accurate to within ± 0.5 cm^{-1} for the sharp heads recorded on the grating spectrographs but in the case of diffuse bands or for low resolution measurements the error may be larger.

Chapter 3 describes the results of our studies on the D—X and the C—X systems of HgCl. The bands of the D—X system of HgCl are violet degraded and most of them show four heads although a few bands with only two heads are also seen. The use of higher resolution and dispersion has enabled us to get well resolved vibrational isotope shifts for Cl isotopes and we explain the four headed structure as being due to the Q and P heads corresponding to the two isotopic molecules $HgCl^{35}$ and $HgCl^{37}$. The mercury isotope heads are however not resolved and only a slight broadening due to this effect is seen in the band heads with $|\Delta v| > 1$. Our vibrational assignments have been verified by comparing calculated and measured chlorine isotopic shifts. The molecular constants have been calculatad using a least squares computer program.

We have been able to partially resolve the rotational structure in the (0,0) and the (0,1) bands of the D—X system. This partially resolved rotational structure has been analysed, assuming it to be due to a $^2\pi_{3/2}$—$^2\Sigma^+$ transition. Considering the spin splitting in the $X^2\Sigma^+$ state and the Λ doubling in the $^2\pi_{3/2}$ state to be negligible least squares computer program was used to fit the wave numbers of the observed rotational lines to appropriate branch equations of a $^2\pi_{3/2}$—$^2\Sigma^+$ transition. The best fit could reproduce the measured wavenumbers to within ± 0.1 cm^{-1}.

The rotational constants for the ground state determined from our final analysis are in good agreement with the constants reported from a study of the B—X system. The observed separation between the Q and the P heads in different bands have been used to estimate α_e thereby permitting an estimate of B_e for the $D^2\pi_{3/2}$ state.

We have also calculated the true (RKR) potential energy curves for the D and the X states and the (Morse) Franck-Condon factors for the various bands of the D—X system. The calculated F. C. factors are seen to be in close qualitative agreement with the observed vibrational intensity distribution.

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The bands of the C—X system of HgCl are also violet degraded. We have observed well separated heads corresponding to the isotopic molecules $HgCl^{35}$ and $HgCl^{37}$. The isotopic shift between the $HgCl^{35}$ and the $HgCl^{37}$ confirms our vibrational assignments. The ground state vibrational constants obtained from this analysis are in good agreement with the constants obtained from the analysis of the D—X system. The constants of the C-State however, differ greatly from the constants reported earlier.

Chapter 4 deals with the ultraviolet bands of HgBr. The bands of the C—X and the D—X systems are violet shaded but the shading of the banbs in the E—X system is not clear. The (0,0) band for both the C—X and the D—X systems is easily recognised as sharp and double headed band. In each case the two heads are very different in their intensity and are attributed to the fine structure effect. In the (0,0), (1,0) and the (0,1) bands of the C—X system and in the (0.0) band of the D—X system we have observed the P and the Q heads separately. For a large number of bands of the C—X system and the D—X system, isotopic heads due to the two bromine isotopes are clearly resolved. The bands odserved in the wavelength range 2700-2770 Å show multiple heads due to the mercury isotopic shifts. The intensity distribution in both the C—X and the D—X systems shows certain anomalous features and we have explained them in terms of calculated F. C. factors.

The bands lying in the 2430-3470 Å region of the spectrum are somewhat diffuse and of low intensity. Besides, the bands assigned earlier to the E-X system a large number of other bands with similar features are also observed in this same wavelength region. These bands could successfully by fitted into a vibrational scheme with almost the same vibrational frequencies for the upper and the lower states as for the E-X system. We have attributed the two groups of bands to the two subsystem of a $^2\pi - ^2\Sigma$ transition implying $a^2\pi$ (case a) character for the E state for which the spin orbit coupling parameter A is estimated to be $= 90\ cm^{-1}$.

The rotational constants for the C and the D states have also been estimated using the separations between the P and the Q heads and taking the rotational constants for the ground state from earlier work. The rotational constants determined in this manner also satisfy the standard isotopic relations for the isotopic molecules ($HgBr^{79}$ and $HgBr^{81}$).

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Chapter 5 describes the results of our study of the ultraviolet bands of HgI. The bands in the C-X and the D-X systems are violet shaded whereas the bands of the E-X system are red shaded. The bands with negative values of $\triangle v$ are sharper than those with positive values of $\triangle v$ in the C-X system. Further one band in each of the $\triangle v = o, -1, +1$ sequences is of abnormally low intensity, though bands on either side of this band appear quite prominently. The band heads in the positive sequences are quite broad and the (2,0), (3,1) and (4,1) bands show several heads. This splitting has been explained as due to the mercury isotope effect and has helped us in confirming the vibrational assignments. Several new and previously unobserved bands have also been observed in our work.

We have succeeded in observing bands involving high values of $|\triangle V|$ in the D-X system. It is found that the 0-1 sequence is the most intense. Many bands appear as broad and diffuse probably due to the unresolved mercury isotope structure. The double heads expected for a $^2\pi - ^2\Sigma$ transitions, as the D-X system has been suggested to be, could not be detected in our work.

In the case of the E-X system the two groups of bands lying in the region 2650-2600 Å and 2600-2540 Å respectively are very similar in structure and it appears that they are the components of a common transition. The (0,0) bands of both the components are very poor in intensity but the two heads due to the multiple structure of the transition are easily identified. The isotopic heads due to the mercury isotopes are not resolved.

As has been stated above we have been able to observe separately the P and the Q heads in the 1-0, 0-0 and 0-1 bands of the C-X system. We have estimated the rotational constants for the C state, assuming it to be a $^2\pi_{1/2}$ state, from the measured head-head separation.

We have also estimated the Morse F. C. factors for the different bands of the C-X system of HgI using these vibrational and rotational constants. These values are in very good qualitative agreement with the observed vibrational intensity distribution.

In Chapter 6 we summarise our findings on the spectrum of diatomic HgX molecules. The applicability of a simplified model of HgX in terms of molecular orbitals arising for Hg^+ has been discussed.

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PHOTOACOUSTIC SPECTROSCOPY OF SOME MATERIALS

Virendra Nath Rai Sup : *Dr. D. K. Rai*

Photoacoustic effect is based on the generation of heat in a sample through non-radiative processes following the periodic illumination and consequent absorption of light by the sample. If the sample is placed in an airtight photoacoustic cell the periodic heat pulses give rise to pressure fluctuations which is detected by a sensitive microphone fitted into the cell. This technique is free from effects of scattered radiation and does not require any special sample preparations for recording the spectra. In the present work, we have carried out the spectral studies in the wavelength range 400 to 800 nm on some powdered solid samples (rare earth oxides), liquids (solution of organic dye) and surfaces (thin film of silver and overlayer of RhB and Rh6G on silver).

First Chapter of the thesis contains a brief theoretical description of the generation of photoacoustic signals from solid samples based on the one dimensional model proposed by Rosencwaig and Gersho. According to this model the air at the interface of solid and gas acts as a piston on rest of the air column and thus generates pressure variations that are detected by the microphone. A brief account of the three-dimensional heat flow is also presented which is capable of explaining some of the observations that are not explained by the one dimensional theory of Rosencwaig and Gersho. The non-radiative relaxation processes have been presented by taking an example of a large organic molecule. Objectives of the present work are summarized at the end of this chapter.

The design, fabrication and parametric studies of an electret microphone are presented in second chapter. The electret diaphragm was prepared from thin mylar sheets after coating one side by silver which acts as one electrode of the microphone. The electret foil was polarised by two methods and measurements were made to optimize the sensitivity of the microphone. The variation in microphone sensitivity has been studied for different thicknesses of mylar sheet, different designs of back plate and different polarization techniques. The decay of microphone sensitivity was also studied as a function of time. A comparison between our home made microphone and a commercial microphone (Sennheiser Electronics) was made by recording the photoacoustic spectra of Nd_2O_3 and PbI_2 using both microphone in the same PAS cell.

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The fabrication of photoacoustic spectrometer using components of Indian origin has been discussed in Chapter 3. Measurements are reported on a fixed wavelength photoacoustic spectrometer that uses the argon ion laser for the source and variation of photoacoustic signal with laser power, chopping frequency, particle size of the samples have been studied. The effects of backing material, channel cross-section between microphone chamber and sample chamber, were also investigated, using carbon black sample. The variation of phase angle with frequency was studied for carbon black and PbI_2.

The wavelength tunable photoacoustic spectrometer has been used to record spectra of CdS, PbI_2, SnS_2 in the powder form which yield band gap as 2.4 eV, 2.5 eV and 2.5 eV respectively in good agreement with literature values. The spectrometer has been shown to work in the reflection as well as transmission mode to record the reflectance and the transmission spectra of solid samples. The transmission spectrum of radiation damaged Kapton foil was recorded and analysed. The spectra of liquid algae and whole blood were also recorded to show the applicability of the spectrometer for different kinds of samples.

In Chapter Four, we report the photoacoustic spectra of the rare earth oxides Ho_2O_3, Er_2O_3, Nd_2O_3, Gd_2O_3, Sm_2O_3, Pr_2O_3 and Tb_2O_3. Strong PAS signals were identified to be from those energy levels of the triply ionized rare earth ions which are either absent or appear weakly in the fluorescence spectra of these compounds studied by earlier workers in the crystalline phase.

Changes in the photoacoustic spectra of Er_2O_3 and Nd_2O_3 were found to occur after irradiation with slow neutrons. The change, is however, found to be reversible after storing the sample under room temperature conditions over a period of one weak. These observed effects tend to indicate creation of defects and change in the oxidation (ionization) state of the ions from Re^{3+} to Re^{2+}.

The photoacoustic spectra of solutions of Rh6G and RhB in ethanol are reported in Chapter 5. Concentration dependent studies of these solutions as well as their mixtures have been made and it is observed that the PAS signal of the mixture in the range 480 to 530 nm is greater than the corresponding signal in either of the dyes alone.

The PAS spectrum of RhB has also been recorded after bubbling O_2 gas through the solution and it is observed that the signal increases with increase in the duration of bubbling and exhibits saturation.

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Chapter 6 contains the results of our investigations on the photo-acoustic transmission spectra of thin films of silver (thicknesses 11 A°, 19 A° and 49 A°) before and after coating it with an overlayer of Rh6G or RhB. It is found that the silver film shows only one peak due to absorption caused by the plasma resonance of the silver particles and that this peak shifts to longer wavelengths with increase in the thickness of silver film. The spectrum of silver film having an over layer of the dye shows the splitting of the resonance peak in two parts. The intensity of the transmission spectrum in this case is different than the intensity for silver film or the dye film alone. These observations have been interpreted in terms of the Maxwell-Garnett theory.

INVESTIGATIONS ON THE THIN FILMS OF BINARY, TERNARY RARE EARTH METAL TRIALUMINIDES (RAl_3, $R_{1-x}R'_xAl_3$) AND RNi_5 INTERMETALLICS

Ajay Kumar Singh Sup. : *Dr. O. N. Srivastava*

The process of alloying occupies a special significance in the science of metals. The formation of solid solutions, intermetallics and electron phases through alloying leads to synthesis of metallic materials whose structure and properties can be tailormade to desired specifications. It is curious to note that most of the metallic materials which have found use in devices are not elemental metals themselves but the alloyed variants of these. Thus warm superconductors such as V_3Si, Nb_3Sn, high coercivity magnetic materials $SmCo_5$, RFe_2, simulated phases representing high pressure phases like SmGdS are all alloys. The significance of alloys is thus obvious. Unlike noble and usual transition metals, rather sparse studies are available for alloys based on rare earth metals. However, very subtle and significant properties are exhibited by rare earth metal alloys. The existence of superconductivity in many rare earth trialuminides (e. g. $YbAl_3$) and the storage of hydrogen at densities higher than liquid hydrogen in rare earth pentanicklides (e.g. $LaNi_5$) are some such examples. Motivated by their special significance as indicated in the foregoing-the present investigation was carried out, the central theme being the growth, synthesis and characterisation of rare earth metals trialuminides and pentanicklides. Some studies covering properties of these alloys was also undertaken.

Rare earth intermetallics represent an important part of the more general problem in metals. They represent the widest range of alloy formation. These intermetallics are known to be of great technological

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importance due to their special magnetic, superconducting and hydrogen storage characteristics. By virtue of their special electronic and crystallographic these intermetallics (particularly RNi_5 intermetallics) absorb hydrogen exothermically, reversibly, nonstoichiometrically and without demanding hydrogen of high purity. Keeping in view the fact that hydrogen has recently been recognised as a substitute for oil (petroleum) a special importance has been attributed to rare earth intermetallics.

These intermetallics have also offered many mysterious and subtle structural transformations induced by high pressures. They also exhibit some interesting structural series in particular the composition RX_3, (R = rare earth metals, X = aluminium). Several attempts have been made to explain these features. However, the situation remains far from being clearly and completely understood.

Noticeably, a large amount of work regarding bulk rare earth intermetallics has been reported but the studies regarding their thin film phases are rather sparse.

The present investigations were aimed at studying the synthesis and structural characterisation of (1) rare earth metal binary trialuminide RAl_3 (R = Gd, Tb, Ho, Dy) in thin film form (2) rare earth metals ternary trialuminides ($R_{1-x}\ R'_x\ Al_3$: $Gd_{0.9}\ Ho_{0.1}\ Al_3$, $Gd_{0.5}\ Ho_{0.5}\ Al_3$, $Gd_{0.1}\ Ho_{0.9}\ Al_3$) in thin film form and (3) rare earth pentanicklides (RNi_5) intermetallics in thin film form with the particular emphasis on their hydrogen storage characteristics.

Studies in regard to (1) and (2) eventually led to the discovery of several modulated phases akin to polytypes. Efforts have been made to explain the genesis and stabilisation of these modulated phases based on the lowering of electronic energies in terms of Fermi surface and Brillouin zone interaction (F. S.—B. Z. interaction).

Studies in regard to (3) suggested that thin films of RNi_5 ($HoNi_5$, $GdNi_5$) have comparatively higher hydrogen storage capacity than the bulk agglomerates.

The thesis has been divided into six chapters. Chapter 1 viz., 'Structure of Metals and Alloys' discusses briefly some general principles of alloy synthesis, equilibrium diagrams, structure of metals and alloys, close packing, polymorphism, polytypism and its theories; factors affecting crystal structure of metals and alloys, Hume Rothery rules, theory of primary solid solubility of alloys, Jones' theory and explanation of Hume Rothery rules. In addition to above, the origin of the long

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period superlattice structures and the relevance of Fermi surface and Brillouin zone interaction in the stabilisation of superlattices and other similar structures have been discussed.

The second chapter deals with the technique of transmission electron microscopy which describes the basic principles and technique with reference to the present investigations. Some of the main topics discussed in this chapter are kinematical theory of electron diffraction and image contrast, two beam dynamical theory, contrast due to various planar interfaces and the salient features of lattice imaging.

The next two chapters (3 and 4) are concerned with the 'investigations on the formation synthesis and characterisation of binary rare earth metal trialuminides ($TbAl_3$, $DyAl_3$, $GdAl_3$ and $HoAl_3$) in bulk and thin film forms with emphasis on the occurrence of modulated phases. These alloys were synthesised through the process of sintering which was initiated by homogenising the powders of rare earth metal and aluminium in the stoichiometric ratio (R:3Al) in vacuum ($\simeq 10^{-6}$ torr) at 500-600° C for 20 hours. The initial agglomerates so formed were tested by x-ray diffraction employing Guinier focussing camera in transmission. The structures of the agglomerates were found to be in excellent agreement with the reported structures. Thin films from these agglomerates were made by thermal vapour deposition in vacuum ($\approx 10^{-7}$ torr). The thickness of the thin films were characterised by using multiple beam interferometry. They were of 300-1000 A° These thin films were characterised through transmission electron microscopy. The imaging (normal and high resolution) and diffraction modes were employed.

The as grown thin films were found to be amorphous as evidenced by the featureless electron micrograph and electron diffraction patterns exhibiting halos. On electron beam heating (pulse annealing), these thin films underwent an amorphous to crystalline transformation. The transformed crystalline phase consisted of single crystals, with planar faults and twins. An extensive analysis of diffraction patterns from these crystals in basal and non-basal orientations revealed the presence of modulated phases which were akin to polytypes. For example the modulated phases which were discovered in the present investigation are 2H, 3C, 4H, 5H, 8H, 9R and 15R for $GdAl_3$, 2H, 4H, 3C, 6H, 8H, 10H, 14H, 6R, 9R, 15R and disordered phases for $TbAl_3$; 2H, 4H, 5H, 15R, 30R, 42R and disordered phases for $HoAl_3$.

The fifth chapter describes the formation synthesis and characterisation of ternary rare earth metal trialuminides $R_{1-x}R'_xAl_3$ (R,R'=Gd, Ho; x=0.1, 0.5 and 0.9) and the occurrence of modulated phases in thin

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films of these alloys. This chapter also embodies the discussion regarding explanation for the occurrence of modulated phases and describes the proposed mechanism. The work regarding ternary trialuminides was particularly done in order to check the influence of the size of rare earth metals on the formation of modulated phases. Indeed, Buschow (1965) has already suggested that the variation of structure along the series RAl_3 in bulk form is influenced by the size of the rare earth atoms. Our observations, however, revealed that even in the same RAl_3 (say either of the alloys $TbAl_3$, $DyAl_3$, $HoAl_3$ and $GdAl_3$) different modulated phases are present and hence the application of his suggestion becomes inappropriate. In order to check specifically the effect of size on this phenomenon, a ternary trialuminides consisting of Gd, Ho and Al corresponding to compositions $Gd_{0\cdot9}\ Ho_{0\cdot1}\ Al_3$, $Gd_{0\cdot5}\ Ho_{0\cdot5}\ Al_3$ and $Gd_{0\cdot1}\ Ho_{0\cdot9}\ Al_3$ were studied. These compositions were chosen to consider the two extreme and also an intermediate compositions. The occurrence of the modulated phases were revealed in the cases of ternary trialuminides as well, e. g. the modulated phases discovered for $Gd_{0\cdot5}\ Ho_{0\cdot5}\ Al_3$ are 4H (ordered and disordered versions), 8H, 15R and 36R. This system had not been studied in bulk phase before.

This chapter also deals with the origin of modulated phases in binary and ternary trialuminides, and describes the reasons why the already proposed theories cannot be applied directly to the present case. A feasible mechanism (proposed mechanism) based on the lowering of electronic energy as a consequence of Fermi surface and Brillouin zone interaction has been discussed. The instability of the as grown amorphous thin film phase is first discussed in terms of Nagel and Tauc model based on nearly free electron theory. Then the formation and stabilisation of the modulated phases are discussed on the basis of lowering of electronic energy. It has been suggested that a variation in the state of amorphosity in the as grown thin film manifested by different values of $\vec{q}_p$ (say $\vec{q}'_{p_1}$ $\vec{q}_{p_2}$....etc.) at which the peak in the structure factor occurs may give rise to different modulated phases with reciprocal lattice vectors (say $\vec{g}_1$, $\vec{g}_2$, . . etc.) which satisfies the condition $\vec{g}_1 = 2\vec{k}_{f_1}$, $\vec{g}_2 = 2\vec{k}_{f_2}$ . . . etc. This is just a mathematical manifestation of the fact that F. S. touches the Brillouin zone. A schematic diagram exemplifying the F. S.-B. Z. interaction has also been suggested for the cases of binary trialuminides. The only requirement for the success of this suggestion is a small variation in the electronic concentration giving rise to a suitable change in F. S. so as to meet the B. Z. boundaries corresponding to the reciprocal lattice vector of large structure factors. This

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variation in the electronic concentration is feasible because of the valence fluctuation of the rare earth metal and/or stoichiometric variation. The above mentioned scheme has been proposed on the basis of nearly free electron model i. e. Fermi surface is taken to be spherical. Some attempts based on realistic Fermi surface—Brillouin zone interaction have also been described.

The sixth chapter deals with the investigations on the formation, synthesis and characterisation of RNi_5 (R=Gd, Ho) bulk and thin films. The RNi_5 intermetallics are important from the solid state hydrogen storage point of view. These were synthesized by melting the stoichiometric mixture of the rare earth metal and nickel in a vacuum sealed silica tube and then homogenising the melted flux at 800°C for about 24 hours. The agglomerate so formed was tested by x-ray diffraction employing the Guinier focussing camera in transmission mode. These corresponded to the reported $CaCu_5$ type structure. The thin films of RNi_5 were obtained by thermal vapour deposition of the agglomerates in vacuum ($\approx 10^{-7}$ torr). The thicknesses of the films employed were between 300 and 100 Å. The as grown thin films were found to be amorphous as was evidenced by featureless electron micrograph and diffraction patterns exhibiting halos. These amorphous films underwent an amorphous to crystalline transformation when subjected to pulse annealing at about 550-600°C. The transformed polycrystalline phase was characterised and was found to tally with the reported $CaCu_5$ structure. The single crystal diffraction patterns revealed the presence of a 4H structure as well. Since the main emphasis here was to monitor hydrogen storage characteristics of the RNi_5 thin films, extensive investigations in regard to the occurrence of the polytypes were not carried out. This chapter also deals with the hydrogen storage characteristics of RNi_5 (R=Gd, Ho) bulk and particularly the as grown thin films. In this study, the hydrogen absorption in the as grown amorphous thin films and the initial agglomerates were studied by electrolytic method through the electrolysis of water. It has been found that the as grown amorphous thin films absorb more hydrogen than their bulk polycrystalline counterpats.

Summarily, the thin films of binary and ternary trialuminides have been found to exhibit modulated phases akin to polytypes and a feasible mechanism has been put forward to explain the accurrence of these modulated phases. As regards the thin films of pentanickelides the hydrogen absorption in the amorphous thin films is found to be more favourable than the crystalline bulk counterparts.

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SOME CASE STUDIES IN ATOMIC COLLISION PROCESSES

Chandra Shekhar Singh Sup : *Dr. D. K. Rai*

A knowledge of the rates of collision processes which occur between electrons and ions on the one hand and neutral atoms and molecules on the other is of great importance in a broad area of Physics. This has become increasingly apparent in recent times in connection with developments involving electric discharges in gases, atmospheric physics and astrophysics. Apart from this applied aspect the subject of atomic collisions is of great intrinsic interest since a study of collision phenomena has been most productive in the elucidation of the structure of matter.

A collision problem can be divided into three different time invervals. During the first interval the incident particle and the scatterer are very far apart (but the distance between the two is starting to decrease) and can be thought of as being in well defined energy states. The interaction (scattering) takes place in the second interval wherein the distance between the two systems is small (comparable to or smaller than the extension of the associated wave packets). In the final interval the reactants (collision products) are again a large distance apart but the internal states (this does include a change in momentum) of the two collision partners have changed. This therefore is a time evolution problem in which an initial state describing the collision partners in their initial configuration evolves to a final state. The probability of observing a certain final state from out of the infinite set of possible states is the quantity of interest to which (Classical or) quantal collision theory addresses itself. In view of the limitations of obtaining an exact analytical solution of a many particle problem in quantum mechanics approximation methods are of paramount interest. Two aspects of the approximations have to be considered. One is involved in the description of the initial and final states of the collision partners and the other is regarding the description of the collision process itself. An unusually simple model is the so called Born approximation-whose applicability and range of validity-though dependent on the specific problem in hand-for high impact energies is well established. A continuing effort to devise improvements in this basic approximation to make it applicable at (low and) intermediate impact energies is going on and several procedures have been devised. In the present thesis some of these approximations have been applied to specific cases and in one of these a modification has been suggested.

In Chapter I we have briefly described several of the approximation methods which are currently in use to describe electron/ion impact

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with atoms/molecules. For example we have discussed briefly the close-coupling and related methods as well as the R-matrix methods which are applicable for low impact energies. Out of the methods used in intermediate and high energy regions we have discussed the method due to Crothers and McCarroll, the first Born approximation, the Glauber approximation, Coulomb-projected Born and related approximations as well as the distorted wave methods. The last two are discussed in Chapters II and III respectively alongwith their applications.

In Chapter II we have discussed the electron impact excitation of helium and helium-like ions using the Variable charge Coulomb projected Born (VCCPB) approximation which is a (in some senses the most) generalized form of the Coulomb-projected Born approximation. Since the VCCPB method is in the general class of the distorted wave (DW) methods we expected these calculations to be similar to results of the other DW models when applied to the specific excitations considered by us. This expectation was fulfilled neither in the case of the He atom nor of the He-like ions. The divergence is especially acute at low impact energies. A comparison of the differential equation satisfied by the radial part of the scattered wave in the VCCPB method with the equation in other DW models shows that though the equations have a fair degree of similarity the manner in which distortion is accounted for in the VCCPB method is inadequate.

In Chapter III we studied the electron impact 2^3S excitation of He in the VCCPB as well as in a 'modified' VCCPB method. In this modified method the prior form of the T-matrix is used. The effect of distortion is included in the final channel wherein the total wavefunction is also completely antisymmetrized. In contrast in the VCCPB method (where the post form is used) the distortion is again considered in the final channel but the total (final channel) wavefunction is used in a simple unsymmetrized form. We find that the changes in the VCCPB approximation as made in our 'modified' VCCPB approximation do improve the results of the VCCPB method. This is not surprising since the 1^1S-2^3S excitation takes place only when exchange contribution is included (in a nonrelativistic calculation) and our modification introduces the Hartree-Fock type exchange potential term in the differential equation satisfied by the radial part of the scattered wavefunction.

In Chapter IV we have studied the collision of electrons and protons with alkali atoms. We have studied the electron impact excitation of the lowest lying autoionizing states in Li, Na and K using the

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Glauber, Crothers and McCarroll's and first Born approximations. Proton impact excitation in the first Born approximation is also considered. Electron impact excitation of the resonance transitions of Li, Na and K has also been studied using the method due to Crothers and McCarroll.

FAST PROTON TRANSPORT IN SOLIDS

Narendra Singh Sup : *Dr. S. Chandra*

Most ionic solids like alkali halides have very low conductivity (10^{-12}—10^{-16} ohm^{-1} cm^{-1}). However, a large number of solids have recently been discovered with high ionic conductivity (10^{-1} - 10^{-4} ohm^{-1} cm^{-1}) comparable to those of liquid electrolytes. These solids are termed as 'superionic solids' or 'soild electrolytes' or 'fast ion conductors'. These have been used to obtain many solid state ionic devices like electrochemical cells or batteries, timers, display devices, pollution control, fuel cells, partial pressure gauges etc. Most of the superionic materials developed are those for monovalent cations with small ionic radii like, Ag^+, Cu^+, Li^+, K^+, Na^+ etc. with the exception of the monovalent anion F^- and divalent anion O^{2-}. Lately, attention has been directed towards monovalent cation proton or H^+ which has smallest cationic radii. Successful development of proton conductors are of great use in fuel cell, hydrolysis cells, high-energy density batteries electrochromic optieal display devices apart from helping the understanding of proton transport in more complex biophysical systems.

Fast proton transport in solids presents special problems. The 'naked' H+ ions are not present in solids since H+ is generally covalently bonded to some electronegative atoms/ions like C-H, N-H, O H etc. Further, in many cases, hydrogen atoms are shared between two electronegative atoms to form directional hydrogen bonds. A necessary step in the proton conduction involves oscillation of H from one side of the hydrogen bond to another. Thus, proton transport would involve at least 'two steps' and the effective activation energy is likely to be large. Further, it is rather tricky to establish unambiguously the proton transport and its likely mechanism in any material (viz., liquid like transport, vehicle and Grotthus mechanisms).

The present thesis tries to establish proton transport in hydrazine sulphate by using a variety of techniques.

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Chapter 1 briefly reviews the recent development in superionic materials. Transport mechanism in normal ionic solids is known to be governed by the movement of point defects (Frenkel and Schottky defects). The high ionic conductioni n superionic solids is mostly due to highly disordered structure and cooperative motion of ions. Different models for superionic phase transitions are described in detail. An overview of the solids which show fast proton transport or high proton conductivity is also given which serves as an introduction to the subject matter of the thesis relating to proton transport in hydrazine sulphate.

Chapter 2 describes the transference number measurements necessary to establish the existence of ion transport in solids. The coulometric technique for measuring proton transport number is described in detail. The principle is based on Faraday's law of electrolysis. When a current is passed between electrodes holding the sample in the form of a pressed pellet, the electrochemical product of the conduction in the form of gas is collected at the -ve electrode and is measured. The percentage of charge carried by the protons is calculated from the volume of the gas collected. For hydrazine sulphate, hydrogen evolution on passing a current through it establishes proton transport. A considerable deviation from straight line behaviour has been found in our experiment due to change in the stoichiometry of the sample after considerable electrolysis has taken place. The initial proton transference number evaluated from the straight line region is approximately one.

Chapter 3 describes the measurement of D. C. and frequency dependent conductivity of hydrazine sulphate in the frequency range varying from 100 Hz to 100 KHz at different temperatures from 300°K to 500°K. The D-C conductivity has been estimated from complex-admittance (B-G) plots. The σ vs. $1/T$ curves show a sudden increase in conductivity at about 480°K which has been attributed to the presence of a structural phase transition. Activation energy has been found to be temperature dependent. The frequency dependence of conductivity has also been found to obey a temperature dependent power law. The temperature dependent activation energy and frequency dependence of the conductivity has been explained on the basis of 'variable-potential-barrier' model. A possible mechanism for proton transport has been suggested.

Chapter 4 describes the nuclear magnetic resonance measurement with a view to study the dynamics of proton motion in hydrazine sulphate, The two different experiments i.e. the linewidth and the relaxation time measurements as a function of temperature help in

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understanding the ion dynamics. The NMR linewidth of hydrazine sulphate shows a line narrowing at a temperature of about 150°K indicating that protons are mobile at temperatures higher than this. A minor hump is observed at a temperature of about 228°K which indicates a possible structural phase transition. The jump attempt frequency has been estimated from Bloembergen, Purcell and Pound relation and it is $\sim 10^{11}$ sec^{-1}. The low attempt frequency is nearly proton tunnelling frequency suggesting H^+ motion. The relaxation time measurements also confirm the above conclusions.

Chapter 5 describes the IR and Raman spectra studies on hydrazine sulphate. IR spectra is a good fingerprint of various structural groups. A comparison of IR spectra of original and electrolysed sample from which some H^+ ions have been transported out of electrolysis in a coulometric experiment is likely to give some idea about the position of mobile species. With this view IR spectra of hydrazine sulphate was recorded for (a) a fresh sample and (b) a sample taken after electrolysis. The IR spectra of electrolysed sample shows, in addition to $-NH_3^+$ vibrations, the bands for $-NH_2$ rocking at 1265 cm^{-1} and $-NH_2$ deformation at 1730 cm^{-1}. It also shows the presence of bands at 1430 cm^{-1} which is due to $N_2H_5^+$ deformation. This suggests that one H^+ ion has been transported from $N_2H_6^{2+}$ ion to form $N_2H_5^+$ ion.

The presence of low frequency modes in laser Raman spectra are also indicative of free ion situation. The laser Raman spectra of hydrazine sulphate shows the presence of a large number of low frequency modes in the region below 200 cm^{-1} apart from the normal vibration. This suggests free ion motion in hydrazine sulphate.

Chapter 6 gives the important conclusions obtained as a result of different experimental observations. The proton transport mechanism in hydrazine sulphate involves the $-NH_3$ group reorientation around N_1-N_2 axis of the hydrazonium ion ($H_3N^+ — {}^+NH_3$) and a proton hopping (or tunnelling) between adjacent molecules of the same group.

EFFECTS OF HIGHER ORDER EXCHANGE IN HEISENBERG FERROMAGNET

Mohan Tiwari

Sup : *Dr. R. N. Srivastava*

The present thesis deals with the study of Heisenberg ferromagnet with higher order exchange. The existence of biquadratic exchange, three and four atomic sites interaction in addition to usual bilinear

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exchange has been experimentally established in different magnetic compounds. Various mathematical techniques like Molecular Field Theory, Spin Wave Theory and High Temperature Series Expansion methods have been used to obtain expressions for magnetic parameters. Green function technique has found wide applications in this field. Theoretical study of Heisenberg ferromagnet with biquadratic exchange using Green function technique has also been carried out. We have used Green function technique to study the effect of higher order exchange interaction on Heisenberg ferromagnet. The effect ef anisotropy has also been discussed. The whole thesis is divided into four chapters. The first chapter gives a general introduction and contains the mathematical technique used in the present investigations. It contains the application of Green function in the field of magnetism and particularly to the Heisenberg ferromagnet. A summary of the work done earlier in the field of interest related to the present investigation has also been given.

The first part of the second chapter deals with the effect of biquadratic and higher order exchange interaction on isotropic Heisenberg ferromagnet. The Hamiltonian for such a system is given by

$$= -_{ij} J_{ij} S_i S_j - _{ij} J_{ij} (S_i S_j)^2$$

the first term stands for usual Heisenberg Hamiltonian and the second term for biquadratic exchange interaction. J is exchange integral constant. S_i and S_j are spin operators of regular lattices i and j. Summation extends over all i's and j's. is biquadratic exchange parameter which measures the strength of biquadratic exchange interaction. It varies from 0 to 1. The origin of the biquadratic exchange interaction in addition to usual linear Heisenberg exchange interaction has been described in detail. Spin wave energies and spectral intensity have been calculated in presence of biquadratic exchange interaction. In addition to bilinear and biquadratic exchange interaction, the effects of higher order exchange interaction e. g. three atomic sites interaction on magnetization and quadrupolar order parameters have been described in the second part of the second chapter. Spin wave energies have been studied at low temperature region. The Hamiltonian of such a system is written as

$$= -_{ij} J_{ij} S_i S_j - _{ij} J_{ij} (S_i S_j)^2 - _{ijk} ijk (S_i S_i) (S_j S_k)$$

The first and second term represent usual bilinear and biquadratic exchange interaction and third term stands for three spin interaction. L is the coefficient of three spin interaction. The origin of these types of interactions have also been discussed. The results have been compared

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with the other theoretical and experimental results. We have studied these effects for regular crystal lattices e. g., sc, bcc, and fcc for spin (S = 1) system.

In first part of the chapter third, the effect of crystal field anisotropy on Heisenberg ferromagnet has been studied. The Hamiltonian of such a system is given by

$$= -_{ij} J_{ij} S_i S_j -_i D(S_i^z)^2$$

Here, the first term is usual Heisenberg Hamiltonian and the second term is due to uniaxial anisotropy. D is the anisotropic parameter and and S_i^z is the—component of spin S on —tb lattice. Here, we have followed the Green function technique of Devlin. However, we have accounted for all possible intersite correlations which have been neglected by Devlin and others. The effect of crystal field anisotropy on Curie temperature has been discussed in detail. The calculation is limited to weak anisotropy, sc and bcc lattice and spin (S=1) system. The second part of this chapter deals with the effect of crystal field anisotropy on Curie temperature fo an anisotropic model which is important from practical point of view. Hamiltonian for such a system is written as

$$= -_{ij} J_{ij} (\tfrac{1}{2} (S_i^+ S_j^- + S_j^+ S_i^-) + S_1^z S_1^z) \\ -_i D (S_1^z)^2.$$

Here, is anisotropic exchange parametsr which varies from 0 to 1, =0 represents Ising and =I Heisenberg ferromagnet. The 1st term stands for anisotropic Heisenberg exchange and the second term is due to single ion anisotropy. This model actually describes the behaviour of magnetic materials between Ising and Heisenberg Ferromagnet. The variation of Curie temperature with crystal field anisotropy for different anisotropic exchange parameter has also been studied.

The first part of Chapter fourth contains the effect of biquadratic exchange on Curie temperature in presence of crystal field anisotropy. The Hamiltonian for such system is given by

$$= -_{ij} J_{ij} (S_i S_j) -_{ij} J_{ij} (S_i S_j)^2 -_i D(S_1^z)^2$$

The first term is bilinear exchange the second one is due to biquadratic exchange and third is due to crystal field anisotropy. The parameters have already been discussed earlier. Here we find that biquadratic exchange an uniaxial anisotropy affect the Curie temperature in opposite fashion, and at certain values of anisotropic parameter the biquadratic exchange shows the annuling effect. In this way, the effect of

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of biquadratic exchange on Curie temperature in presence of uniaxial anisotropic parameters.

The second part of this chapter deals with anisotropic Heisenberg model. Hamiltonian in this case in written as

$$= - \sum_{ij} J_{ij} \left(\tfrac{1}{2} S_i^+ S_j^- + S_j^+ S_i^-\right) + S_i^z S_j^z$$

$$- \sum_{ij} J_{ij} \left(\tfrac{1}{2} (S_i^+ S_j^- + S_j^+ S_i^-) + S_i^z S_j^z\right)^2$$

$$- i D(S_i^z)^2.$$

The first term is due to anisotropic exchange, the second term stands far bequadratic exchange with anistropy and the third is due to uniaxial anisotropy. In this model the effect of exchange anisotropy parameter on Curie temperature with uniaxial anisotropy in presence of biquadratic exchange have been studied.

The result obtained by Green function technique followed in the present work have been compared with those obtained by the application of Molecular field theory, Spin Wave Theory and High Temperature Series Expansion Methods. The results have also been compared with the experimental results.

HIGH RESOLUTION STUDIES ON ELECTRONIC BANDS OF SOME DIATOMIC MOLECULES (CP, SbO, SbO^+, CuBr)

Ramayana Tripathi Sup : *Dr. K. N. Upadhyay*

Spectroscopic investigations of molecule provide informations on the motions of electrons and nuclei and the interaction amongst them. The transitions from one electronic configuration to another are characterized by the band spectra in the visible and UV regions. When these spectra are observed at higher resolutions, it is possible to obtain data on changes in molecular geometry while going from one electronic configuration to the other by measuring the corresponding lines arising due to the rotational motion of the nuclei. At very high resolution it is possible to observe effects produced by nuclei due to their mass, volume and spin. In the present thesis we are concerned with the studies of the spectra of diatomic molecules in the UV and visible regions recorded on instruments of medium and high resolutions. The vibrational bands photographed with medium resolution have been analysed to give the

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vibrational frequencies and anharmonicities in the two combining electronic states. High resolution spectra have been analysed rotationally to obtain the equilibrium internuclear separations as well as the centrifugal distortion constants. It has been possible to identify and analyse the rotational structure due to different isotopic species of the same molecule.

The whole work presented in the thesis has been divided into five chapters. Chapter 1 deals with the general theory of diatomic molecules in brief which is necessary for the work presented in the following chapters. The methods of rotational analysis of electronic bands using the graphical as well as the least squares procedure have also been described in this Chapter.

The rotational analysis of $B^2\Sigma+-A^2\pi_1$ system of the CP molecule has been presented in Chapter 2. The analysis of this system of CP molecule reported by previous workers seems to be doubtful in the light of recent work on the isoelectronic molecules. The emission spectrum was recorded in the 2nd order of a 10.6m concave grating spectrograph and the rotational structures in the red degraded (0,0) and (1,1) bands have been analysed. These bands were excited in the transformer discharge with a small amount of white phosphorus in the middle and a small amount of grease near the neck of the tube facing the spectrograph. All the six branches expected in the structure could be marked easily in all three bands. The J assignments to the lines have been made by comparing the combination diflerences among themselves and with the B-X system. A precise molecular constants including B_e value (not known earlier) have been determined for both the electronic states. It is found that the spin splitting constant (γ) in the $B^2\Sigma^+$ state has a negative value which is in accordance with the γ-value in $B^2\Sigma^+$ states of other isoelectronic molecules. This differs from the value reported by the earlier workers both in magnitude as well as in sign. The present analysis also suggests that γ-value for the ground electronic state of CP must be positive.

Chapter 3 contains the rotational analysis of the $B^2\Sigma^+ - X^2\pi_{3/2}$ transition of SbO molecule. This system (3400 – 4500 Å) has been a subject of extensive study for several years. All the previous studies (Lakshman (1960), Singh et al. (1967), Chakoo et al. (1978) and Verma et al. (1978) on this system are found to be of doubtful nature in the light of the work on C-X and D-X system of this molecule. The rotational structure of (0,0) and (1,0) bands (reddegraded) of this system photographed earlier in the 2nd order of the 10.6 m concave grating spectrograph (0.33 Å/mm reciprocal dispersion) has been analysed accurately.

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The constants for the $X^2\pi_{3/2}$ state as estimated with the help of the constants of $X^2\pi_{1/2}$ do not agree with the constants reported earlier. It has also been found that the previous workers have wrongly assigned the P_{Q12} branch as P_2 and in most of the cases J assignment (Singh et al. 1967) is also found to be incorrect. The present identification has been confirmed by the relative intensity estimate of various branches wherein, it has been found that the intensity of $Q_2 > PQ_{12} > P_2$ and so on

The spin splitting constant (γ) for $B^2\Sigma^+$ state of SbO is found to be appreciable with negative sign. However, it was also marked by Chakoo et al. (1978) but the magnitude was less and sign of γ was positive. The magnitude and sign of γ have been confirmed by comparing them with the γ-value reported for $B^2\Sigma^+$ state of isoelectronic molecules (PO and AsO). The structure due to $Sb^{121}O$ and $Sb^{123}O$ have marked clearly in the photograph.

The spectrum of SbO^+ in emission has been photographed in the 2nd order of the 10.6 m concave grating spectrograph and forms the subject matter of Chapter 4. The bands were excited using 2450 MHz Microwave Oscillator having 125 watt power with the sample Sb_2O_3 kept in the bulb of an electrodeless Quartz discharge tube. The rotational structure in (1,2) and (1,3) bands has been analysed for the first time.

There are only six branches present in the structure which shows that three branches are due to $^{121}ScO^+$ and the other three are due to $^{123}SbO^+$. It indicates that the transition is of the type $\Delta\Lambda = \pm 1$. The J assignment is made by comparing the combination differences for the excited states. The presence of negligibly small combination defect confirms that the excited state of the transition must be a $^1\pi$. Threrore the assumption of ground state to be a $^1\Sigma^+$ by Chakoo and Patel seems to be correct. The molecular constants were determined by both graphical as well as least squares procedure. The internuclear distance and vibrational frequency in the ground state of SbO^+ are compared with the respective constants in the ground state of SbO. It is found that these ratios are in good agreement with the ratios obtained in similar molecules ($\frac{NO^+}{NO}$, $\frac{PO^+}{PO}$, $\frac{AsO^+}{AsO}$).

Chapter 5 contains the results of vibrational analysis of the CuBr spectra. It is divided into two parts. Part A deals with vibrational analysis of some new bands in the red region whereas part B deals with

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the vibrational analysis of some new bands in the green region. The bands were photographed in the first order of the 10.6m concave grating spectrograph with 0.7 Å/mm reciprocal dispersion and ~180000 resolution. Natural $CuBr_2$ has been used to get the emission bands in the hollow cathode d. c. discharge. All the bands are violet degraded. The vibrational analysis of red system of CuBr has been confirmed by isotopic shift calculation. A tentative vibrational analysis of the bands in the green region of CuBr spectra has been made on the basis of the vibrational isotopic shift calculation. These analysis have led to the identification of at least three new electronic states for which vibrational constants have been determined for the first time.

VIBRATIONAL STUDIES OF SUBSTITUTED TRIFLUOROMETHYL BENZENES

Ram Anjore Yadav Sup : *Dr. I. S. Singh*

The present thesis would include the vibrational spectral studies of the following molecules :

(1) o-, m- and p-trifluoromethyl benzaldehydes

(2) o-, m- and p-trifluoromethyl benzonitriles and

(3) p-trifluoromethyl aniline.

The polarised Raman spectra of these compounds were recorded in the region 50-4000 cm^{-1} on a Jobin Yvon Ramanor HG. 2S spectrometer using the 5145 Å line of an argon-ion laser as the source of excitation. The near infrared spectra of the seven compounds were recorded in the region 200-4000 cm^{-1} on a Perkin-Elmer-621 spectrometer and the far infrared spectra were recorded in the region 33-700 cm^{-1} on a Beckman IR-11 spectrometer.

The observed frequencies in the Raman and infrared spectra are assigned to different fundamental modes. To check the proposed vibrational assignments normal coordinate analysis has been performed for each molecule using Wilson's G-F matrix method. General Valence Force Field was used to calculate the fundamental frequencies. Good agreement has been achieved between the observed and calculated frequencies.

The thesis would be divided into six Chapters. After giving a brief introduction in Chapter I, Chapter II describes briefly the experimental and theoretical procedures. Chapter III contains the vibra-

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tional studies of o-, m- and p-trifluoromethyl benzaldehydes. In this Chapter, the internal modes of the CF_3 and CHO groups are discussed in detail. It is observed that the CF_3 and CHO group modes are strongly coupled with the phenyl ring modes and the CF_3 and CHO group modes interact even in para position of the substituents. Some of the interesting phenyl ring modes like the ring breathing, trigonal C-C-C in-plane bending, Kekule vibration etc. modes are discussed in detail.

The vibrational spectra of o-, m- and p-trifluoromethyl benzonitriles have been discussed in Chapter V. In this Chapter the CF_3 group and phenyl ring modes are discussed briefly. In the case of o-, m- and p-trifluoromethyl benzonitriles, the C N group modes have nearly same frequencies and it appears that the interaction between the CF_3 and CN groups modes is negligibly small.

Chapter V deals with the vibrational spectra of p-trifluoromethyl aniline. The NH_2 group modes have been discussed in detail and the phenyl ring modes briefly. It is observed that the NH_2 group modes (except the scissoring and rocking modes) are localized within the NH_2 group.

The last and the VI Chapter summarises the results of the vibrational studies of the seven molecules discussed in Chapters III, IV and V. In this Chapter the CF_3, CHO and CN groups modes are compared and the effect of the CHO and CN groups modes on the CF_3 group modes in the ortho, meta and para positions has been discussed. Some of the ring modes are also summarized in this Chapter.

The assignments of the CF_3 group modes for all the seven compounds are fairly consistent. The force constants are found transferable from one molecule to other to a good extent.

THE LIMITING BEHAVIOUR OF PROBABILITIES IN SOME OCCUPANCY PROBLEMS

Badri Prasad Sup : *Dr. V. V. Menon*

In the classical occupancy problem, distinguishable balls are distributed independently and at random in m distinguishable cells. The problem has been studied extensively. Recently, the following generalization of the problem has attracted attention (called the "randomized

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occupancy problem") : after the balls are distributed, each ball has a probability $p(0<p\leqslant 1)$ of staying in its cell and a probability $1-p$ of falling through the cell. The variables which have been studied are

W_k (m, p) = number of balls dropped until the kth cell becomes occupied for the first time;

$M_0(n,m,p)$ = number of empty cells obtained after n balls are dropped.

The numbers k, n and p are allowed to vary with m. Clearly, the case $p=1$ corresponds to the classical problem.

We are interested in the limiting behaviour of W_k and M_0 as $m\to\infty$. A survey of the known results may be found in Johnson and Kotz (*Urn Models and Their Applications*, Wiley, 1977). For example, in the case $p\neq 1$, nothing is known except the limiting distributions of W_k and M_0 (found by Samuel—Cahn, *Ann. Prob.*, 2 (1974). From the survey in Johnson & Kotz (1977), Chapt. 6, we find that for the classical case $p=1$, the limit laws of W_k were found by Baum & Billingsley, while some more information (e. g., a local central limit theorem) on the limiting behaviour of M_0 has been obtained by Rényi, Kolchin, Békéssy, etc. Moreover, although the behaviour of $P[M_0 = r]$ has been studied frequently in the classical case, the literature is silent regarding the behaviour of the distribution function $P[M_0\leqslant r]$.

To be specific, consider the central limit theorem for M_0. Denote the mean of M_0 by $E(M_0)$ and the variance by $V(M_0)$, and

$$u = \{r-E(M_0)\}/\sqrt{V(M_0)},$$

$$\phi(u)=(2\pi)^{-\frac{1}{2}}\ e^{-u^2/2};\quad \Phi(u)=\int_{-\infty}^{u}\phi(t)dt.$$

The central limit theorem states that, for fixed u,

$$\lim_{m\to\infty} P[M_0\leqslant r]=\Phi(u). \qquad (1)$$

The local central limit theorem, which is more difficult to establish, states that

$$\lim_{m\to\infty} P[M_0=r]/\{(V(M_0))^{-\frac{1}{2}}\ \phi(u)\}=1. \qquad (2)$$

The result (1) was proved by Rényi for the classical case $p=1$ (he showed that (1) holds iff $V(M_0)\to\infty$, where n/m may tend to O, const., or ∞), and by Samuel—Cahn for the randomized case $p\neq 1$. The result

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(3) was proved for the classical case ($p=1$), under the condition that n/m does not tend to zero or ∞, by Kolchin.

In practice, since n and m will be finite (though large), it is more useful to study the remainders R_1 and R_2 for large but finite m, where

$$P[M_0 \leqslant r] - \Phi(u) = R_1,$$

$$P[M_0 = r] / \{(V(M_0))^{-\frac{1}{2}} \phi(u)\} - 1 = R_2.$$

For, example, a result of the form $R_1 = O(1/\sqrt{m})$ is informative in the sense that it gives us an idea of the *rate of convergence* in (1), on the other hand, a result of the form $R_1 = (G(u)/\sqrt{m}) + 0(1/m)$ is much more useful because it also gives us the better estimate $\Phi(u) + (G(u)/\sqrt{m})$ for F(r), as compared to the simple estimate $\Phi(u)$. Such estimation of R_1 ann R_2 we call the *problem of normal approximation*. When the limit law is Poisson. we have similarly the *problem of Poisson approximation*.

In the present thesis we tackle the problems of the normal and Poisson approximations to $W_k(m,p)$ and $M_0(n,m,p)$. In other words, estimates for the remainders R_1 and R_2 are found, when the normal and Poisson limits hold. Most of our results are new also for the classical case $p=1$.

LIMITING PROBABILITY DISTRIBUTION IN SOME URN MODELS WITH INDISTINGUISHABLE BALLS

N. K. Indira Sup. : *Dr. V. V. Menon*

Urn models, where one studies arrangements of "balls" or "particles" in "urns" or "cells", play an important role in discrete probability theory. Various examples can be found in text books of elementary probability theory, while an excellent survey is given in the book *Urn Models and Their Applications* by Johnson & Kotz (J. Wiley, 1977). Models with distinguishable balls, specially, the behaviour of cell occupancies (e. g., Classical occupancy problem, Maxwell-Boltzmann Statistics) have been studied extensively. On the other hand, models with indistinguishable balls do not seem to have attracted similar attention.

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Consider the distribution of *n indistinguishable particles into m cells*. There are two models, called the *Bose-Einstein Statistics* :

(I) cells are permitted to be empty, and $\binom{m+n-1}{m-1}$ distinguishable arrangements are regarded as equally probable;

(I*) no cell is allowed to be empty, and the $\binom{n-1}{m-1}$ distinguishable arrangements are regarded as equally probable.

In Model I, define the random variables

M_k = number of cells containing exactly k balls each.

N_k = number of cells containing at least k balls each and similarly the random variables M_k^*, N_k^* in Model I*.

In the present Thesis, we study in detail the limiting behaviour of the random variables M_k, N_k, M_k^* and N_k^*, when $m \to \infty$ and n/m behaves in different ways.

The first step is to identify *all* the possible limit laws of the above variables. It is shown (Chapter 2) that the possible limit laws are degenerate, or Poisson, or Normal. The Normal limit law arises when $n/m \to$ const. $\neq 0$, whereas the other limit laws arise when $n/m \to 0$ or ∞. Many of our results are new.

The next step constitutes a more challenging and interesting problem, which we have called the *problem of Normal approximation*, formulated as follows. To be specific, consider the r. v. M_k, and suppose that under suitable conditions, and with suitable quantities a_m and b_m, the Central Limit Theorem holds for M_k, i. e.

$$(1) \qquad \lim_{m \to \infty} P\left[\frac{M_k - a_m}{b_m} \leqslant x\right] = \Phi(x) \text{ for each fixed } x,$$

where $\Phi(x)$ is the d. f. (distribution function) of the standard Normal. Consider the difference

$$(2) \qquad P\left[\frac{M_k - a_m}{b_m} \leqslant x\right] - \Phi(x) = R_m(x).$$

Eq. (1) gives us the limiting value (namely, zero) of the 'error' $R_m(x)$. How does $R_m(x)$ behave for any large but finite m ? Is it possible to find an *estimate of* $R_m(x)$? A similar problem arises with the pr. f. (probability function) of M_k, if the local Central Limit Theorem holds. This is the problem of Normal approximation. Any answer to the

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problem gives us an idea of the rate of convergence to the Normal law. Further, it provides us with an estimate $\Phi(x) + R_m(x)$ for $P[(M_k - a_m)/b_m \leqslant x)$ which is clearly superior to the estimate $\Phi(x)$ given by (1).

The question arises as to whether similar estimates can be obtained for the "error" when the limit law is Poisson. This we call the *problem of Poisson approximation.*

The problems of Normal approximation to the pr. f. and to the d. f. of all the above random variables have been solved in Chapters 5 and 6 of the Thesis, while the problems of Poisson approximation have been examined in Chapters 3 and 4.

As is well known, the Central Limit Theorem is generally easier to establish because general methods are available (e. g., method of moments or characteristic functions). If the random variable being considered is a sum of independent random variables, there is a general method using characteristic functions for proving the local Central Limit Theorem and to solve the problem of Normal approximation.

Unfortunately, the random varriables M_k, N_k, M_k^* and N_k^* cannot be expressed as a sum of independent random variables. However, it is known that their distribution can be expressed as a conditional distribution involving independent random variables and their characteristic functions can be represented as a suitable complex integral. We have used such a representation to tackle the problem of Normal approximation. On the other hand, satisfactory solution to the problem of Poisson approximation is obtained through a method due to Menon.

The problem of Normal and Poisson approximations for Bose-Einstein Statistics have not been studied in the literature till now.

The approximations to the pr. f. and the d. f. obtained by us have been illustrated in Chapter 7. In order to reduce the bulk of the Chapter, we have restricted our attention to M_0 and M_2. Extensive computations were also performed in order to examine a related problem, namely, how large should m be as that the pr. f. and the d. f. of M_0 and M_2 can be estimated by the corresponding function of the relevant limit law (Poisson and Normal) ? Some rough general conclusions could be drawn which are presented in the last Chapter.

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SOME STOCHASTIC MODELS AND THEIR UTILITY TO DESCRIBE BIRTH INTERVAL DATA

R. N. Mishra Sup : *Dr S. N. Singh*

Current rapid growth rate of global population has attracted considerable attention of researchers to understand the process of human reproduction. Mathematical models for human reproduction process, where several biological factors act and interact, are important and indispensable instrument and enable the researchers to identify the factors underlying the phenomenon. Stochastic Models for birth intervals have been one of the tools to study the behaviour of fertility parameters relating to reproduction process. This thesis embodies formulation of stochastic models for describing the data on different types of birth intervals based on some simplified assumptions of human reproduction process.

There are six chapters in the thesis. Chapter I is introductory which presents a brief discussion of the variables of human reproduction and highlights the use of study of various types of birth intervals through stochastic models. A description of the contents of the subsequent chapters a long with a brief review of the development of stochastic models for birth intervals is also given in this chapter.

Chapter II is concerned with the derivation of truncated model for the first birth interval where the females are exposed to risk of conception at different points of time since marriage. The model has been applied to various sets of observed distributions taken from the Surveys "A Demographic Survey of Varanasi (Rural) 1969 and "Rural Development and Population Growth—A Sample Survey 1978" conducted by the Demographic Reserch Centre Banaras Hindu University.

Chapter III deals with the formulation of the truncated probability model for the first birth interval taking fecundability to be a function of time and the fact that different proportions of females are exposed to the risk of conception at different points of time since marriage. The methods to obtain maximum likelihood estimates of the parameters are outlined. The model is applied to some observed distributions taken from the surveys mentioned above.

Chapter IV deals with a probability distribution of any order of closed birth interval to females of a specified marital duration assuming that all the females are not exposed to the risk of conception immediately after marriage. The model takes into account the variation in the non-susceptible period associated with a live birth. The

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application of the model is illustrated with some observed distributions of the survey "A Demographic Survey of Varanasi (Rural) 1969 conducted by the Demographic Research Centre, Banaras Hindu University.

Chapter V is associated with the derivation of some probability models for open birth interval. In one of the models we have assumed that all the females are not exposed to the risk of conception just after marriage. The variation in the non-susceptible period associated with a live birth is accounted. The application of one form of the model is illustrated with one set of data taken from the survey described in Chapter IV.

Chapter VI is concerned with the formulation of some probability models for straddling birth interval based on varying sets of assumptions. The application is illustrated with one set of data taken from the Survey described in Chapter IV.

SHRINKAGE ESTIMATION TOWARDS AN INTERVAL IN LIFE TESTING PROBLEMS

K. N. Singh Sup : *Dr. B. N. Pandey*

The present thesis "Shrinkage Estimation Towards an Interval in Life Testing Problems", consists of six chapters. In this thesis, we have considered a variety of shrinkage methods of estimation about the parameters of some failure time distributions used as models in life testing experiments.

The first chapter presents a brief account of the life testing problems and summary of the works described in subsequent chapters.

Chapter II deals with the problem of estimation of normal population variance using 'shrinkage techniques' in case a priori information about σ^2 is available in the form that σ^2 lies between σ_1^2 and σ_2^2, which are known values. The proposed shrunken estimators are based on known and estimated shrinkage factor. The expressions for mean squared errors of these estimators are obtained. The proposed estimators are compared with the minimum mean squared error (MMSE) estimator, in terms of mean squared error. It is shown that the proposed estimators are preferable to MMSE estimator in some guessed interval of the parameter space of σ^2.

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In Chapter III, a variety of shrinkage methods have been proposed for the estimation of scale parameter of an exponential distribution by considering estimators based on a priori interval containing the parameter. In the first two sections of this chapter, the proposed shrunken estimators are based on known weighing factor. In the last section, the proposed estimators are based on estimated weighing factor. The expressions for mean squared errors of these estimators are obtained. It is shown that the proposed estimators are better than the MMSE estimator in some guessed interval of the parameter space.

In Chapter IV, we have considered the shrinkage estimation of variance θ^2 in an exponential distribution when some guessed or prior values of θ^2 is available in the form of an interval (θ_1^2, θ_2^2), which contains θ^2 in it. The proposed shrunken estimators are developed for a known and estimated weighing factor. We have obtained the expressions for mean squared errors of these estimators. The proposed estimators are compared with the usual estimators in terms of mean squared error. It is shown that these estimators have smaller mean squared error than the usual unbiased estimator $\frac{n}{n+1}x^2$ in some guessed interval of θ^2. Chapter V proposed some shrunken estimators for the shape parameter β of Weibull distributioon under censored sampling when some a priori or guessed interval containing the shape parameter β is available. The proposed estimators are based on known and estimated weighing factor. We have obtained the expressions for mean squared errors of these estimators. We have compared all these estimators, in terms of mean squared error, with the usual unbiased estimator. We have also shown that these estimators have smaller mean squared error than the usual unbiased estimator β in some guessed interval of the parameter space of β.

In Chapter VI, we have considered Bayesian shrinkage estimation of scale parameter θ of an exponential distribution when information regarding θ is available in the form of a prior distribution. We have considered the case in which prior distribution places a weight (1-b) in the guessed value θ_0 and distributes rest of the probability mass b according to some probability distribution. First we have obtained a Bayes estimator θ_0 for a given prior distribution. Next we have combined the usual unbiased and maximum likelihood estimator x and the Bayes estimator θ_0 on the lines of shrinkage technique. We have also studied the properties of the proposed estimators.

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SOME FERTILITY MODELS AND THEIR APPLICATIONS

Usha Srivastava Sup : *Dr. S. N. Singh*

The specific role of stochastic models is to provide a clear insight into the action and interaction of several biological factors that affect human fertility. In the last three decades, a large number of researchers have been engaged in building up mathematical models for the number, timing and sequence of conceptions, births, etc. under varying sets of assumptions. The limitation of these models in relation to their applicability becomes largely evident, when viewed against their restrictive assumptions. In this study we have proposed some probability models which are more realistic than those developed earlier. The present study has been divided into five chapters.

Chapter I is introductory, which highlights the use of stochastic models for human fertility in demographic studies. It also includes a summary of the contents of the subsequent chapters, along with a brief review of the suggested models and also of the previous work done in this direction.

Chapter II is concerned with the derivation of a model for first birth interval with the consideration that females may not be susceptible to conception at the time of marriage for a random interval of time because of certain social and biological constraints. The model is derived on the assumptions, among others, of limited time for observation and consideration of the finite nature of the non-exposure period. The model has been applied to different sets of observed distributions.

Chapter III deals with the presentation of a probability model to describe the variation in the number of conceptions to women during T years since marriage. In this chapter the random interval of non-susceptibility, following marriage, is brought under consideration, as in the previous chapter. The model is applied to two sets of data.

Chapter IV is concerned with the development of a probability model with a view to describing the distribution of conceptions to females within a given time period, when the start of the observational period is a distant point since marriage. In the derivation of the model allowance is made for the onset of secondary sterility during the observational period. For illustration, the model is applied to two sets of observed distributions.

In Chapter V, while investigating the number of conceptions during T years, given that the commencement of the observational

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period is a distant point since marriage, a bivariate probability distribution is derived. In derivation of the model the factor of onset of secondary sterility during the observational period is also considered. The application of the model is illustrated through one set of observed data.

In all the chapters, the data are taken, whenever needed, from the survey entitled "Rural Development and Population Growth—A Sample Survey 1978)" which was conducted under the auspices of Demographic Research Centre of Population Studies, B.H.U., Varanasi.

The author believes that the models presented in this thesis are useful for understanding of the complex nature of human fertility. The study is thus expected to be of help and assistance to the researchers engaged in deriving more realistic models for the phenomenon.

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ZOOLOGY

COMPARATIVE EVALUATION OF COMMON SEROLOGICAL TESTS FOR SPECIES AND GROUP IDENTIFICATION (*BLOOD GROUP ANTIGENS*) OF THE BIOLOGICAL FLUID STAINS

Arun Kumar Bapuly Sup : *Dr. G. P. Agarwal*

So many tests are available to the Forensic Serologists for species and group identification of biological fluid stains. Most applied techniques for species identification are Ring-precipitin, (R. P.), Gel-diffusion (G. D.) and Gel-electrophosis (G. E.) techniques and for group identification, Agglutination-Inhibition (A. I.), Mixed-Agglutination (M. A.), Absorption-Elution (A. E.) and Passive-Haemagglutination (P. H.). A review of literatures revealed the fact that no comparative account had been done on specificity and sensitivity of the techniques, in relation to the increasing age and dilutions of the stained materials, of different biological fluid stains and also of blood group substainces which were most effected under ABO (H) typing of the biological fluid stains, with the increasing age and dilutions.

In the present study, 100 samples each of Blood, Semen and Milk (of human origin) were collected and 10 cm. X 10 cm., 100 stained and dried samples of each were prepared. Controlled samples (50) were collected from Goat, Sheep, Cow/Bull and Buffalo. The stained samples with complete information were kept in polythene bags inside the cupboard, for two years and the tests for species and group identification were carried out after 1 week, 2 weeks, 1 month, 2 months, 4 months, 6 months, 8 months, 10 months, 1 year and 2 years.

A. Techniques for species identification :

(i) Ring-Precipitin Technique (R. P.) :—The extracts of stained materials of Blood, Semen and Milk in 0.89% saline had been prepared for 1/20 to 1/20000 strength and kept seperately in tapering and test tubes. The corresponding antiserum was run slowly to get the antiserum settles down at the bottom of the test tube and were left for one hour on the work bench. The controle sex were also set simultaneously. The positive results were indicated by the formation ring at the juncture of the Antigen (Extract) and corresponding antiserum and the ring did not form in the controle.

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(ii) Gel-diffusion Technique (G. D.) :—The extraction of the stained materials was done in gel-buffer and various dilutions of the extracts were made (as done in R. P. Technique) in gel-buffer, both for experimental and control samples.

The G. D. slides were prepared by pouring hot 1% Gel-solution in gel buffer on a slide and allowed to cool down to solidify the gel-layer. One central and 6 Equidistant and equal sized peripheral wells were cut, the antiserum and various dilutions of the extract were placed in the central and 6 peripheral wells, respectively and the slides were kept in a moistened chamber for 72 hours in a refrigerator. The possitive reaction was indicated by the formation of a precipitin band in between the antiserum (central well) and antigen (extract contained in peripheral wells), while in the control no band appeared. The slides were washed, dried and stained for final reading.

(iii) Gel-electrophoresis Technique (G. E.) :—The extraction of the stained materials were done in gel-buffer and various dilutions of the extracts were prepared in gel buffer for experimental and control samples.

The G. E. slides were prepared by pouring hot 1% gel solution in gel-buffer on a slide and allowed to cool down to solidify the gel layer. 6 sets of wells (2 wells in a set), equal sized and equi-distant wells were cut on a slide. 6-8 slide thus prepared were placed in side the electrophoresis through containing electrode buffer and the current was passed to stabilize the set, soon after the power was cut off and the various dilutions of the extract were placed in the cathodic wells and the antiserum in the anodic wells. The electrophoresis was carried out for a total period of two and half hours. The precipitin bands (indicating possitive result) appeared in between the cathodic (extract and anodic (antiserum) wells and no band (indicating negative result) appeared in case of controls. The slides were washed, dried and stained for final reading.

Comparing the sensitivity and specificity of the free techniques (R. P., G. D. and G. E.) for Blood semen and Milk stains, it is concluded that the G. E. technique followed by R. P. and G. D. techniques, gave the highest mean values of possitive result with the Blood stained at all the ages and dilutions of the stained extract.

The G. E. technique followed by the R. P. and G. E. techniques, gave highest mean value of positive result with the seminal and milk stains at all the ages and at all the dilutions of the stained extract,

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so out of the three techniques the G. E. technique is the most specific and sensitive one and is followed by R. P. and G. D. techniques. Similarly, the stains at all dilutions gave the highest mean values of positive result followed by seminal and milk stains. This shows that out of the three fluid stains, the blood stains are most stable, followed by seminal and milk stains, respectively.

B. Techniques for group identification :

(i) Agglutination-Inhibition Test (A. I.) :—In each of the three tubes one drop of the particular dilution of the extract (as mentioned in R. P. technique) was taken and then one drop of antiserum (anti-A, anti-B and anti-O (H) lectin) was added separately in each of the three tube respectively. The tubes were incubated for 4 hours in a refrigerator and subsequently 1 drop of the corresponding indicator cell suspension was added to each tube. The positive result were indicated by the absence of agglutination of the corresponding indicator cells while in the negative results the agglutination of the indicator cells took place.

(ii) Mixed-Agglutination Test (M. A.) :—On fibre of the stained material was taken in each of the three tapering end test-tubes, one drop of anti-A, anti-B and anti-O (H) lectin was added seperately. The tubes were incubated for 3 hours in the refrigerator and then washed with 0.89% chilled saline solution by centrifugation. Subsequently one drop of corresponding indicator cell suspension was added in each tube. The positive result was indicated by the appearance of the agglutination of the indicator cells while the negative result were indicated by the absence of the agglutination of the indicator cells.

(iii) Absorption-Elution Technique (A. E.) :—One fibre of the stained material was taken in each of the three tapering end test tubes and one drop of anti-A, anti-B and anti-O (H) lectin was added separately to each one. The tubes were incubated for 4 hours in a refrigerator. Subsequently the fibres were washed with chilled 0.89% saline, then to each tube, 1 drop of corresponding indicator cell suspension was added and incubated in a water bath at 56°C. for 12 minutes. The fibres were immediately removed from the tubes and the tubes were left on the working table for half an hour. In case of positive reaction agglutination of the indicator cells was observed while no agglutination was seen in negative reaction.

(iv) Passive-Haemagglutination Technique (P. H.) :—0.5 ml. of the various dilutions of the stained extract and 0.5 ml. buffer saline with 1 ml., 4% Tanned red cell suspension were incubated at 30°c. for

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10 minutes, separately. Subsequently 50% cell suspension out of this was prepared.

One drop each of the cell suspension was taken in three different tubes with one drop of the anti-A, anti-B and anti-O (H) lectin, respectively. Tubes were left at room temperature for half an hour. Positive result were indicated by the appearence of the agglutination of the red cells while negative result was indicated by the absence of agglutination of the indicator cells.

By making an overall comparison of the result of all the four techniques for three different fluid stains, it is concluded that;

The 'A' possitive samples are most stable, followed by 'B' positive, 'O' positive and 'AB' positive samples, for all the three fluid stains. Out of the four technique employed, the M. A. technique is most sensitive and specific, followed by A. E., P. H. and A. I. technique, depending upon the percentage of positive results for each Blood group possitive samples. Out of the three fluid stains, the Blood stains most stable with the increasing age and dilution of the stain extract followed by seminal and milk stains, respectively. The percentage of positive results fall for all the Blood group positive samples of Blood, semen and milk stains with the increasing age and dilutions of the stained materials for all the four technique.

SOME BIOCHEMICAL HISTOCHEMICAL AND ELECTRON MICROSCOPIC STUDIES IN CARCINOMA OF THE CERVIX UTERI

Ashwi Birdi Sup : *Dr. S. Gupta*

The present study was conducted on 457 histologically proved cases of squamous cell carcinoma of cervix. These cases were subdivided into different clinical stages (depending upon the spread of tumor), morphologic degree of differentiation within the tumor and clinical radiation response (CRR) groups following radiotherapy. The parameters studied were :

Group I : Biochemical Parameters—included serum copper level (SCL), serum LDH isoenzymes, leucocyte alkaline phosphatase (LAP) and plasma histaminase.

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Group II : Histochemical observations-were made on mast cells, acid and alkaline phosphatases (ACP and ALP), glycogen and acid and neutral mucopolysaccharides (AMP and NMP).

Group III : Electron microscopic study-included semithin and ultrathin section study.

1. (a) *Serum copper level (SCL)*—Mean SCL in 106 cases was significantly raised in comparison to 55 healthy age matched female controls. The raised SCL lowered significantly following successful radiotherapy. Though there was a trend of elevation of SCL with the clinical progression of the disease, this change was not significant in successive clinical stages. Similarly there was no relation of SCL with the morphologic degree of differentiation. But following radiotherapy mean SCL was significantly more in small cell non-keratinizing carcinoma as compared to large cell variety. SCL was found to be significantly more in poor clinical radiation response (CRR) group following radiotherapy as compared to good and moderate CRR groups. In cases of local recurrences SCL was found to be significantly more in comparison to controls. Thus SCL can serve as an indicator of successful radiotherapy and can be used as a simple check parameter for recurrences.

1. (b) *Serum LDH isoenzymes*—study on 106 cases revealed that principle activity was confined to LDH-2 and LDH-3 fractions with a significant rise of LDH-2 in comparison to controls. Following radiotherapy a significant fall was observed in LDH-2 and LDH-3. There was no consistent pattern of LDH isoenzyme distribution in different clinical stages and morphological differentiation within the tumor. In the cases showing good and moderate CRR LDH-2 and LDH-3 were lowered significantly following radiotherapy while in poor CRR group there was no such significant change. The distribution of LDH isoenzymes seems to be an important prognostic parameter.

1. (c) *Leucocyte alkaline phosphatase (LAP)*—activity was determined in 140 cases. The mean LAP score was significantly low in comparison to controls. Following successful radiotherapy LAP scores returned within normal range. Mean LAP scores were found to be independent of clinical stages. Moderately significant low mean LAP score was observed in small cell non-keratinizing carcinoma as compared to large cell variety. Following

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radiotherapy LAP was significantly low in poor CRR group when compared with good and moderate CRR groups. Low LAP scores has got some diagnostic value and can serve as a parameter to assess clinical radiation response.

1. (d) *Plasma histaminase*—activity was estimated in 79 cases. The mean plasma histaminase was significantly higher in these patients as compared to controls. The raised value fell significantly following radiotherapy. There was no consistently significant change in plasma histaminase activity in successive clinical stages. However, post-treatment values were significantly more in stage III and IV as compared to stage I and II. Significantly higher values were observed in keratinising carcinoma as compared to large and small cell non-keratinising carcinoma. Following radiotherapy there was a significant change of plasma histaminase activity in large and small cell variety while in keratinising carcinoma no such change was observed. Pre-treatment plasma histaminase activity was more in moderate and poor CRR groups as compared to good CRR group. After radiotherapy values were significantly lowered in good and moderate CRR groups though there was no change in poor CRR group. Plasma histaminase reflects the degree of differentiation and can be of immense help in assessing the treatment response.

2. (a) *Mast cell*—study done on the same group as that of plasma histaminase estimation, have shown that mast cell distribution, as few and many, was unrelated with plasma htstaminase values. Similarly, it had no bearing with plasma histaminase in different clinical stages and morphological types. Mast cell distribution as such was also unrelated to clinical stages. Many mast cells were found in majority of the cases of large cell non-keratinising carcinoma as against small cell variety. Further in good CRR group 72.41% of cases had many mast cells as against 42.10% in poor CRR group. Though mast cells have no correlation with plasma histaminase activity but they can serve as an indicator of differentiation and radiation response.

2. (b) *Acid phosphatase* (*ACP*)—activity observed in 110 cases, was present in cancer cells bearing from + to + + + +. It was absent in stroma. ACP appeared to increase with the clinical progression of the disease. Further it was found to be more in small cell variety than in large cell variety. In normal squamous epithelium only basal cells were weakly positive for ACP. ACP can be diagnostic of malignancy.

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2. (c) *Alkaline phosphatase* (*ALP*)—activity was found to be negative in cancer cells except in 12 cases out of 110 where mild to moderate ALP activity was seen. Stroma was found to be rich in ALP. ALP activity was seen only in clinical stages III and IV. Further ALP activity was present in small cell non-keratinising and keratinising carcinoma.

2. (d) *Glycogen*—contents as indicated by diastase digestion were either negative or weakly positive in all the 110 cases of carcinoma cervix. Distribution of glycogen contents in cancer cells were unrelated to the clinical stages. Glycogen contents diminished as the tumor dedifferentiates. The presence of glycogen seems to be associated with the maturation of squamous cell carcinoma as it was richly positive in non-cancerous eyithelium.

2. (e) *Acid mucopolysaccharides* (*AMP*)—All the cases of squamous cell carcinoma (110) had + to + + + AMP contents in the stroma of the tumor. It was found to be increased with the clinical progression of the disease and as the tumor dedifferentiates. It probably helps in defense against the spread of the tumor.

2. (f) *Neutral mucopolysaccharides* (*NMP*)—contents were weakly positive irrespective of clinical stages and morphological degree of differentiation.

3. (a) *Semithin section study*—was found to be useful in studying the nuclear and cytoplasmic details. Nuclear abnormalities, inclusions, cytoplasmic changes, dark and light cell phenomenon could be better studied in these sections. They serve as an excellent opportunity for simultaneous study of light and electron microscopic studies in the same area and comparison could easily be made.

3. (b) *Ultrastructural findings*—Electronmicroscopic study was done in 4 cases of large cell non-keratinising and 2 of small cell non-keratinising carcinoma. For comparison tissues were taken from normal cervix. Changes observed at ultrastructural level in cancerous tissues were mainly nuclear and cytoplasmic changes. Nuclear changes observed were marked irregularity of shape, pleomorphism of chromatin pattern, distribution of perichromatin and interchromatin granules in nuclear matrix, thickening of nuclear envelope, variation in nuclear pores, enlarged, multiple and marginated nucleolus, pseudoinclusion and nuclear bodies of diverse morphology. Amongst cytoplasmic changes were few defective, swollen, pyknotic and pleomorphic

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mitochondria with short, blind, blunt and peripherally placed cristae, poorly developed rough endoplasmic reticulum, numerous polyribosomes lying free in cytoplasm, dilatation and vesiculation of rough endoplasmic reticulum, poorly developed golgi complex and annulate lamellae, various lipid inclusions of variable sizes and density, few lysosomes and abundant tonofilaments, few of them looping through the plaques of desmosomes. Desmosomes were either few or lacking. Extra cellular matrix contained interrupted collagen fibre, elastic fibres, remanants of dead cells and few endothelial cells. Degenerative cells were showing pyknotic and karyorhhectic changes. These changes at ultrastructural level were not specific for carcinoma of the cervix uteri rather they show fundamental changes of neoplasia in squamous cells.

STRUCTURAL AND FUNCTIONAL ANALYSIS OF CHROMATIN OF THE BRAIN OF THE RAT AS A FUNCTION OF AGE

Madan Mohan Chaturvedi Sup : *Dr M. S. Kanungo*

Brain is a post-mitotic tissue. It contains unique population of poly (A+) mRNAs (as compared to other tissues like the liver and kidney), particularly during development. Furthermore, the effects of aging processes are more pronounced in this organ due to its post-mitotic nature. The present study was undertaken to analyse the structural and functional changes that may occur in the chromatin of the brain during aging.

Digestion of chromatin DNA was carried out by endonucleases, micrococcal nuclease (MNase), pancreatic DNase (DNase I) and restriction endonuclease Eco RI to probe the conformation of chromatin. Isoschizomeric restriction enzymes, Msp I and Hpa II, were used for determining methylation of DNA. Functionally active conformation of the chromatin was measured by nick-translation. Further, assay of template-engaged RNA polymerase II was carried out to measure the transcriptional efficiency of the chromatin. The contribution of post-translational covalent modification of histones, such as phosphorylation and acetylation, in the maintenance of conformation of the chromatin was also studied.

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Digestion of purified nuclei of cerebral hemispheres of young-adult (18-23 week, for brevity called young) and old (90-119 week) rats by MNase was carried out. The kinetics of digestion, as measured in terms of both DNA made acid soluble and release of mononucleosomes as a function of time, are the same for both the ages. The repeat length of DNA measured from MNase digests is~180 bp for both the ages. This may be because no qualitative and quantitative changes occur in histone H_1 in both the ages. This indicates that the conformation of the chromatin at basic chromatin fibre (100 Å array of nucleosomes) does not change with age.

On the other hand, digestion by DNase I shows that chromatin is less digested in old age. However, here again the basic nucleosomal organization observed from the bands representing multiples of 10 bases is the same for young and old rats. Only the frequency of digestion of exposed cutting sites by DNase I is lower in the old. It may be because of progressively increasing interaction of DNA, histones and NHC proteins that may occur after DNA synthesis stops at very early stage of development and the cells become terminally differentiated. This may make the chromatin more compact with progressive age. Such condensation may occur at or above the level of 30 nm fibre because the pattern of bands representing mono-and oligonucleosomes obtained by MNase digestion is not altered.

The initial rate of digestion by DNase I is faster in the young. Since DNase I attacks initially at the active regions of chromatin, particularly in the sequences flanking the coding region (hypersensitive site), these sequences may be masked by increasing condensation as a function of age. Cell specific expression of specific genes is controlled by DNase I hypersensitive sites and control elements in the active chromatin. Less digestion seen in the old may be due to a decrease in the available hypersensitive sites (regulatory sites) in old age. Consequently, the expression of genes may decline in old age.

The average base pair length (Lbp) produced by Eco RI is not significantly different when nuclei are digested overnight. Supercoiling of DNA in the chromatin produces torsional constraint which is released on extensive digestion. Consequently, chromatin may acquire an open conformation. Therefore, chromatin in the young is in a more open conformation (organisation into domains) which may facilitate more transcription in the young).

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The digestion pattern of purified DNA by Msp I is the same for both the ages. A sharp band of 5.1 kb is observed in both the ages which is absent in Hpa II digestion. This represents a repeatitive DNA fragment in which internal cytosine is methylated (5'C^{m}CGG 3'). This may have a role in differentiation and development of the brain. Comparison of Msp I and Hpa II digestion patterns in both the ages shows that a large proportion of the 5'CCGG 3' sequences is methylated in both the ages. However, methylation is more in the old. Less methylation in the yovng may account for more open conformation and hence greater expression of genes.

Nick-translation of nuclei following DNase I digestion shows lower incorporation in old age. This may be because of less active conformation (hypersensitive sites) and more condensed state of chromatin.

Nick-translation of nuclei following Eco RI, Msp I and Hpa II digestion (quantitation of nicks) gives lower incorporation in the old. The degree of difference in the incorporation is the same when the duration of nick-translation is increased. Since the chromatin is packed in a higher order structure and the cleavage sites of these enzymes are randomly distributed, it is likely that these sites get masked as the chromatin undergoes condensation with increasing age. These enzymes are large (unlike MNase), and may not easily penetrate the fibre and recognize their cleavage sites. These observations support the earlier conclusion that the chromatin gets increasingly condensed with increasing age in post-mitotic tissues.

The assay of template-engaged RNA polymerase II (responsible for hnRNA synthesis) shows that transcription is lower in old age. This may be due to less active conformation. Addition of exogenous eukaryotic RNA polymerase II (wheat germ) does not restore the level of transcription of the old to that of the young. This reiterates the view that not only that active regions of chromatin are less in old age, but also that conformational changes in chromatin occurring during aging may impair the rate of transcription.

Covalent modifications of histones, hyperphosphorylation (produced by $ZnCl_2$) and hyperacetylation (produced by Na-butyrate), do not have any detectable effect on the conformation of chromatin as seen by digestion by DNase I and MNase. It is likely that either most of the modifications are not crucial for conferring nuclease sensitivity, or if any alteration in the conformation has occurred, it is not detected by nuclease digestion. The role of modifications of histones, therefore, may

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only be to maintain the conformation which has been brought about by other effectors/molecules (NHC proteins ?).

The above studies for the first time provide substantial evidence for (a) conformational changes and (b) possible alterations in the control regions of active genes, that occur in the chromatin of the cerebral hemisphere of the rat as a function of age. Such changes may impair expression of genes and lead to aging of the organism.

PHEROMONAL INFLUENCES ON THE OESTROUS CYCLE OF THE LABORATORY MOUSE

Bhushan Kumar Gangrade Sup : *Dr. C. J. Dominic*

The investigations included in the Thesis centre around the primer pheromonal influences on the oestrous cycle and ovoimplantation in laboratory mice belonging to the Parkes (P) strain. It was demonstrated that the disruption of the oestrous cycle in unisexually grouped mice is primarily due to the incidence of pseudopregnancy. It was also shown that the pheromonal stimulus involved in the induction of oestrous cycle irregularities is present in the urine/excreta of females. The present investigations suggest that physical contact between females is essential for the grouping-induced cycle irregularities. Gonadectomised females as well as males are effective in inducing cycle irregularities in intact test females. The results suggest that the production of the oestrous cycle disrupting pheromone is not dependent upon ovarian hormones.

The male induction of oestrus (the Whitten effect) was effected in unisexually grouped females by short-term exposures to conspecific males. Unisexually grouped females maintained short and regular oestrous cycles in the presence of males. Intact females bearing ectopic pituitary transplant in the renal capsule exhibited prolonged (pseudo-pregnancy-like) cycles. These females, in contrast to unisexually grouped females, failed to show cycle shortening following male exposure obviously due to the inability of male pheromone to override the gonadotrophin-inhibiting effect of prolactin secreted by the pituitary grafts. Diet restriction induced disruption of the oestrous cycle in individually housed females. However, the presence of a conspecific male helped to maintain normal oestrous cycles in underfed females to some extent. It is suggested that the presence of a male stimulates hypophysial gonadotrphic activity in underfed females.

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Regularly cycling individually housed females anointed with artificial scent exhibited oestrous cycle irregularities. Linkewise, individually housed females made anosmic by intranasal irrigation with $ZnSO_4$ also showed cycle irregularities. These findings suggest the importance of olfactory cues of non-social origin in the maintenance of normal ovarian cyclicity in mice. Perfumed females housed in unisexual groups failed to show the male induction of oestrous (the Whitten effect). $ZnSO_4$-irrigated females likewise failed to exhibit cycle shortening following exposure to males. Ablation of the vomeronasal organ (VNO) from females in unisexual groups did not abolish the oestrous cycle irregularities. VNO-ablated females in unisexual groups exhibited the Whitten effect following the male exposure. The findings suggest that the male urinary pheromone causing the Whitten effect is volatile and acts through olfactory pathways.

Adrenalectomy of females failed to prevent the grouping-induced disruption of oestrous cycle. Adrenalectomised females also responded to male exposure by exhibiting the Whitten effect. The results suggest that the adrenals are not involved in the induction of oestrous cycle irregularities, and in the male induction of oestrus in female mice.

The involvement of contact stimuli in the male induction of oestrus (the Whitten effect) and the male-induced implantation failure in newly inseminated female mice (the Bruce effect) was evaluated. The results suggest that the pheromone involved in the Whitten effect is volatile (air-borne) and the pheromone involved in the Bruce effect is nonvolatile and acts through contact. These findings indicate that the pheromone involved in the Whitten effect is distinct from the pheromone involved in the Bruce effect.

EFFECTS OF PLANT AND SYNTHETIC JUVENOIDS IN SOME INSECTS

Ram Lakhan Katiyar Sup : *Dr. K. P. Srivastava*

The thesis deals with the effects of plant and synthetic juvenoids in some insects. The work is divided into three chapters : the first chapter deals with the extraction and screening of plant extracts, the second chapter, with the effects of a synthetic juvenoid (ethyl 9-cyclohexyl-3, 7-dimethyl-2, 4-nonadienoate) on a hemimetabolous insect, *Dysdercus koenigii* and third chapter, with the effects of this hormone on a holometabolous insect, *Papilio demoleus*.

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Extraction and screening of plant extracts

Extracts of 36 so far untested aromatic plants belonging to 15 families were obtained by steam distillation of the leaves, flowers, or rhizomes and tested on *D. koenigii*. Four of the extracts were found to have juvenoid, 1 anti-juvenoid, 34 ovicidal and 12 insecticidal properties, some of them with overlapping properties. The most potent juvenoid was found to be present in *Callistemon lanceolatus*, anti-juvenoid, in *Ageratum conyzoides* (cultivated), ovicide in *Citrus limon* (geraniol) and insecticide in *Allium sativum*.

Juvenoid properties of the oil of C. lanceolatus

This oil showed two important properties of a typical juvenoid viz., morphogenetic and gonadotropic.

Morphogenetic effects—The oil inhibited metamorphosis and produced three categories of juvenilised stages : adultoids, imperfect and perfect supernymphs. The structures that get juvenilised are the wings, legs, cuticular pigmentation and genitalia. Besides, it produced certain gonadal derangements like detachment of ovaries on one or both sides, loss of efferent genital duct complex (spermatheca, spermathecal and accessory gland along with genital chamber or vagina) and reduction in the number of mature oocytes.

Gonadotropic—Allatectomy in young adult females inhibited ovarian development but application of the oil of *C. lanceolatus* reversed this effect showing the gonadotropic property of this oil. This was further tested by electrophoretic technique where in it was found that the oil induced vitellogenin synthesis in allatectomised insects.

Effects of synthetic juvenoid on D. koenigii

(I) *Effects on morphogenesis*

Its effects were tested on the III, IV, V instar nymphs and adults.

(1) The treated III and IV instar nymphs undergo their moults normally but produced juvenilised stages at the imaginal moult as a carried over effect.

(2) the V instar nymphs treated up to day 3 produced 4 categories of juvenilised stages: adultoid-I and II, imperfect and perfect supernymphs. After day 3, the JHA failed to produce any external effect but affected the female reproductive organs up to day 4. Beyond this day the insects becomecompletely insensitive to JHA.

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(II) *Effects on the female reproductive organs*

As in case of the oil of *C. lanceolatus*, the JHA produced the following effects :

(1) Uni—or bilateral detachment of ovaries

(2) Loss of the efferent genital duct complex in bilaterally detached ovaries

(3) Reduction in the number of mature oocytes and narrowing of the ovariolar pedicels.

Possible cause of the above

Ovidectomy and ovary implantation experiments spread over the duration of the V instar showed that : (1) the gonadogenital pathway communication (communication between the ovaries and lateral oviducts) was essential during the first three days of the nymphal life for the normal development of the ovaries. The JHA seems to cause disruption of the lateral oviduct(s) at any time during the nymphal life. Disruption up to day 3 seems to cause ovarian immaturation and disruption thereafter, no effect so that when the juvenilised adults (imperfect supernymphs) are opened up, both conditions of ovarian maturity are encountered.

(III) *Gonadotropic effect*

Allatectomy in young adult females inhibited ovarian development but application of JHA in allatectomised insects induced ovarian development and normal oviposition indicating its gonadotropic property.

(IV) *Effects on fecundity and fertility*

Both fecundity and fertility of the adult female are reduced by the JHA treatment. Their causative factors have been discussed. This happened also when the treated males are mated with the untreated females, possibly due to transfer of the juvenoid during copulation or by male sterility or by both.

Effect of JHA on Papilio demoleus

(i) *Morphogenetic effects*—V (ultimate) instar larvae and pupae treated with JHA produced 6 categories of juvenilised stages in case of the larva : pupoid-I and II, larval-pulal intermediate-I and II, larvoid and superlarva and 5 categories in case of the pupa : adultoid-I and II, pupal-adult intermediate-I and II and pupoid. Two new terms, larvoid and pupoid, have been introduced for descriptive convenience.

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(ii) *Prolongation of instar duration*—JHA treatment prolonged the instar duration by 1-3 days in the larva and by 1-2 days in the pupa depending on the dose employed.

(iii) *Ecdysial failure*—In many cases, more particularly at low doses of JHA treatment, eventhough a new cuticle is formed below the old one, the latter does not rupture resulting in an ecdysial failure. Such insects on becoming prepupa show vigorous body contractions occasionally causing ejection of the rectum or rectal prolapse.

Effects on internal organs

Wing discs—The wing discs pass through four stages : prelacunar, lacunar, tracheolated and evaginated during their development which are completed by the prepupal stage. Adult form of the wings is achieved during the first half of the pupal life.

While JHA prevents evagination and full development of the wings, it fails to retain them at the fully larval level of development even in the superlarva.

Brain—The brain is small with rounded lobes in the early V instar, the lobes become slightly conical by day 4 due to differentiation of optic lobes which enlarge by day 5 (prepupa). Further enlargement and differentiation in these parts continue throughout the pupal life.

JHA treatment does not allow the brain to proceed beyond the condition found in the pupoid.

Alimentary canal—Alimentary canal is a straight broad tube in the larva, metamorphosing into adult form in the pupa.

JHA treatment does not allow it to develop beyond pupa 1 day stage.

Silk glands—The paired silk glands are about 80 mm roughly 'S' shaped tubes, degenerating in the prepupal stage.

JHA treatment prevents degeneration ond maintains the glands.

Gonads—Testes are small red coloured bean-shaped widely separated structures in the larva, coming closer in the prepupa and fusing in the pupa.

The ovaries are small reddish structures in the prepupa and mature by the end of the pupal stage.

On JHA treatment both testes and ovaries remain level, the former not fusing and the latter not producing mature oocytes.

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Effects on reproduction

Fecundity and fertility of the adults emerging from the JHA treated larvae and pupae are reduced, 70-90% of adults from the former (but not from the latter) becoming fully infecund.

Fecundity and fertility also decreased when JHA was applied directly on the adult females.

Ovicidal effect

Ovicidal effect of the JHA was investigated by two different procedures viz., by applying the hormone on the adult females of *D. koenigii* and by applying it directly on the eggs of *P. demoleus*. Applied on the female, high dose of the hormone rendered all the eggs nonviable and low dose inhibited embryogenesis both in early and late stages. Applied on the eggs, the effect of the hormone as judged from the increase in percentages of the egg-hatch, larval survival and the larvae reaching adulthood declined with the increase in age of the eggs.

CYTOGENETICS OF MAMMALIAN SEX CHROMOSOMES

Indrajit Nanda Sup : *Dr. Rajiva Raman*

Despite enormous karyotypic diversity the mammalian X-chromosome has ramained unchanged in its DNA content and type of the genes (5% of the genome; conservative size). On the other hand the Y-chromosome in general has been miniaturised to highly sex-specific properties losing in the process, most of the structural genes and comprising predominantly of hetero-chromatin. Little homology is likely to be left between these gonosomes. However, in certain mammals, mostly rodents, the size of X-chromosome is altered owing to the addition of constitutive heterochromatin resulting into another type of sex chromosomes, composite sex chromosomes. The reason for such selective addition of enormous amount of functionally trivial DNA into the particular set of chromosomes is still enigmatic. In this investigation, we have endeavoured to look into the gross structural organisation of composite sex chromosomes in order to derive its functional significance that could be implicated on sex chromosome differentiation in general. Thus the present study has been carried out : (a) to study the nature and organisation of heterochromatin in the composite X and Y chromosomes, (b) to enumerate the possible homology, if any, between them

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and to formulate, (c) the possible modes of origin of these composite sex chromosomes.

In this context we have selected a few Indian rodents and one insectivore which are known to have additional heterochromatin in their sex chromosomes (*M. meltada*, *R. blanfordi*, *M. dunni*, *B. bengalensis*, *K. indica*, *S. murinus*). Of these *Millardia meltada* and *Suncus murinus* have been studied in greater dedail. This study is further extended to the conservative sex chromosome systems like those of house mouse, house rats and *R. cutchicus* in order to get an overview of amount of heterochromatin associated with sex chromosomes and having them, as a point of reference to evaluate the degree of homology between the composite sex chromosomes. In addition, Y-autosome translocation systems of the Indian mongoose have been investigated to identify the Y-chromosome component and check its behaviour in mitosis as well as meiosis. A similar study has been carried out in Indian muntjac which is endowed with X-autosome translocation. In the somatic cells, the chromosomes have been subjected to different banding techniques to identify the regions of heterochromatin. They have then been stained with base-specific fluorochromes so that their molecular organisation could be revealed. Also, the pattern of their replication has been investigated. Apart from banding studies of the somatic chromosomes, patterns and extent of their synapsis during early meiosis have also been investigated. Experiments are conducted to evaluate the likelihood of recombination between the composite sex chromosomes. The results, inferences and speculations obtained from this investigation are briefly summarised as follows.

The C-banding analysis in these species reveals that the large sex chromosomes, possess varying amount of constitutive heterochromatin. In *Millardia meltada* ($2n = 50$), the nearly metacentric X and large acrocentric Y can be unequivocally identified by C-band staining. In the X-chromosome, the centromere and entire short arm are C-band positive. *R. blanfordi* and *R. cutchicus* have the same diploid number (36) with all acrocentric chromosomes except the Y in *R. blanfordi* which is a medium sized subtelocentric chromosome. In the X-chromosome of *R. blanfordi* besides the centromere, the region adjacent to it is C-band positive whereas in *R. cutchicus* having conservative X-chromosome, only centromere is C-band positive. In *M. meltada* as well as *R. blanfordi*, the centromeric heterochromatin stains distinctly darker than the rest of the C-band positive chromosome arm. In both these species the Y-chromosome is totally C-band positive. In *M. dunni*, the whole short arm and the telomeric part of the long arm of X-chromosome are C-

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band positive without displaying a heterogeneity in the staining intensity seen in other two species. Instead, the Y-chromosome shows differential staining intensity after C-banding, its distal region stains distinctly darker than the rest of the chromosome. *B. bengalensis* and *N. indica* possess X-chromosome with varying length of heterochromatic arm (short arm in *B. bengalensis* and long arm in *N. indica*. The Y-chromosome, a medium-sized acrocentric in *B. bengalensis* and second largest subtelocentric in *N. indica* is totally heterochromatic.

The composite chromosomes of musk shrew (*S. murinus*) however, do not possess the extra amount of C-band positive heterochromatin as seen in other species. Eevn the Y-chromosome, which is known to be comprised of heterochromatin in most of the mammals, is not entirely C-band positive. Only the pericentromeric and regions adjacent to both short and long arm are marked to be C-band positive. On the other hand the X chromosome has blocks of heterochromatin on distal part of both long as well as short arms.

Structural analysis of the sex chromosomal heterochromatin in different species under reference was done by (a) Trypsin-Giemsa staining of somatic metaphases and (b) staining with AT and GC base specific fluorochromes viz., Hoechst 33258 and Olivomycin. The G-band pattern turns out to be identical in the heterochromatin of X and Y chromosomes in each species. The band-by-band similarity could be obtained in the short arms of X and Y chromosomes of both *Millardia* and *Suncus*. In the species where distinct banding patterns could not be discerned, the homogeneity has been inferred from their overall staining pattern, which again was similar in both the chromosomes (*B. bengalensis* and *N. indica*). Most notable situation is in *M. dunni*, where the telomeric prominent C-band remains G-band negative in both X and Y chromosomes. The similarity of G-band patterns of X and Y is further confirmed by base specific fluorescence which are characteristic for individual species. Olivomycin responding heterochromatin, which showed dull fluorescence with Hoechst 33258, was marked in *Millardia* in which the short arm heterochromatin of X and entire Y are relatively GC rich. Similarly, the centromeric heterochromatin of *R. blanfordi's* X-chromosome is GC rich, but the heterochromatin contiguous with it is AT rich. So is the heterochromatin of Y AT rich DNA is also present in *Bandicota*, *Nesokia* and *M. dunni*. In *M. dunni*, however, the telomeric heterochromatin of the long arm of X and Y is found to be GC rich. On the other hand in *S. murinus* the centromeric heterochromatin of Y is GC rich (Olivomycin bright) while the X-chromosome heterochromatin of long arm and nonC-band long arm of Y is AT rich.

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Both banding as well as fluorescence studies are suggestive of structural and organisational homology between the increased chromatin of the sex chromosomes at the gross cytological level. Whether, this close similarity indicates their homology, has been checked by observing the extent of synaptonemal complex formation in surface spread meiocytes with the help of silver staining.

That the organisational homomorphism is a reflection of molecular similarity has been depicted from the formation of extensive synapsis during meiotic prophase. In *Millardia*, *M. dunni*, *Suncus*, *R. blanfordi*, extensive synapsis between the heterochromatic segion of XY pair has been checked from the C-banded metaphase-I pictures where the heterochromatic arms of X and Y are oriented in and end-to-end fashion Intererstingly, in *Mus dunni*, a distinct asynaptic region within the paired region has been marked and when compared with the C-banded pictures of somatic chromosomes it is found that the light stained area just above the bright telomeric heterochromatin of Y loops out from corresponding region of X. However, this extensive synapsis between the sex chromosomes contrasts with conservative types, where only minimal regions are found to be involved in synapsis (Mouse, Rats, *R. cutchicus*). Comparision of XY association between the closely allied species *R. blanfordi* (composite XY) and *R. cutchicus* (conservative XY) reveals that while only end-to-end association occurs in the latter extensive synapsis is marked in the former. This finding shows that increased region of synapsis comprises heterochromatin only.

In musk shrew, the sex chromosomes also undergo "lamp brush" like organisation during meiotic prophase which is subsequently resolved into chiasmatic association. This feature is unique to *Suncus* where the sex chromosomes become out-of-phase with reference to autosomes during their synaptic process assuming "lamp brush" organisation prior to chiasma formation. Thus it is envisaged that "lamp brush" stage may signify a chromatin change that may have a role in their organisation for recombination.

Nesokia indica and *Bandicota bengalensis* which have polymorphic sex chromosomes display various non-specific associations between the gonosomes. In *B. bengalensis*, majority of meiocytes have telosynapsis. In *N. indica*, both autologous as well as heterologous association is most prevalently marked among meiocytes. Whether these patterns of association are different substages of pachytene or specific to individual cell could not be established. However, corresponding to the meiotic prophase, two types of metaphase-I plates are encounte-

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red, one with terminally attached XY bivalent, which may have resulted from heterologous association and the other with separate X and Y chromosomes (univalents) which might have originated from autologous association.

In spite of the substantial synapsis in the composite sex chromosomes, the presence of a chiasma in the sex bivalent could be detected only in *S. murinus*. Here, one interstitial chiasma is marked between the distal portions of the short arms of X and Y chromosomes. In all others, the sex bivalents are associated end-to-end. C-band study of the metaphase-I plates of different species show that while it is the short arm of *M.* meltada which is engaged in synapsis with Y, in *M. dunni* the darkly stained C-band region of the telomere of the long arm of X and Y are paired.

The possibility of recombination in sex chromosomes of *M. meltada* has been checked by *in vivo* ^{3}H-TdR treatment during penultimate premeiotic S phase. Another indirect approach of detection of repair activity during zygotene/pachytene has been devised to check the recombination potential. However, both these experiments could not establish any positive evidence for recombination. In the former experiment clear cut isolabelling between chromatids could not be resolved between the sex bivalents. Nonetheless, a few grains were recorded on sex vesicle in DNA repair experiment. The observation suggests that the recombination is precluded in these species.

In almost all instances the Y is entirely heterochromatic. Interestingly in *S. murinus*, unlike in other mammals, the Y is not wholly C-band positive. Both BrdU and ^{3}H-TdR experiments have shown the late replication property of the non C-band region of the Y-chromosome. And it is this region which actually becomes out-of-phase with rest of the genome. At the first hand, it suggests that constitutive heterochromatin as a rule, need not be the latest one to terminate their replication. Besides, it suggests to us that perhaps late replication of primeval Y might have been the initial stage of Y-chromosome differentiation. Further differentiation for establishment of Y-chromosome would be the complete heterochromatinisation which is subsequently manifestated as C-band region.

The late S replication pattern in the female of *M. meltada* and *R. blanfordi* shows that the constitutive heterochromatin of the two Xs also replicate asynchronously. Interestingly, the heterochromatin of "Lyonised X" is later to terminate than its homologue. It is not clear to us whether a variegation type of effect follows from Lyonised region of the X to its constituting portion.

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In the multiple sex chromosome system (Y-autosome translocation) of the Indian mongoose it has not been possible to identify with certainty the Y-chromosome component and the autosome to which it has been translocated. By employing the surface spreading technique of meiocytes we have observed the X-Y synapsis in *H. auropunctatus* and *H. edwardsi*. The pachytene karyotype reveal the 9th pair of autosomes as the carrier of Y-chromosome component.

The sex chromosomes of the mongoose do not show sex vesicle like structures during pachytene. It appears that the loss of heterochromatin from Y may have a role to play in it, i.e., the sex chromosomal heterochromatin may be involved in the sex vesicle like orientation.

The possibility of recombination between the conservative X and Y chromosomes provides the most plausible explanation for the concomitant increase of qualitatively alike heterochromatin in the composite sex chromosomes. Alternatively, displacement of the pairing segment of one of the homologues from the telomeric to interstitial region, in the primitive sex chromosomes may have led to unequal crossing over, products of which could have initiated the process of evolution of the composite sex chromosomes.

LIPIDS IN EPIDERMAL MUCOUS SECRETIONS OF CERTAIN FRESH-WATER TELEOSTS

Ghanshyam Das Nigam Sup : *Dr. A. K. Mittal*

Epithelia are bounding tissues and are usually physiologically active. Many epithelia have a multiplicity of function and this is especially true of the skin epithelium, the epidermis of aquatic animals. Epidermis has to be protective and sensitive, interactions with the environment involve the transport across it of various substances, either actively or passively.

Fish epidermis can generate copious epidermal secretions—the "mucus", which is slowly but continuously dissipating into the surrounding medium. Mucus is at the boundary, or interface of the epidermis and its environment and upon discharge perform diverse functions. The term "mucus" which, in general, is employed for the secretion of a specialized cell—the mucous cell, is used in the present context for a

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variable overlay of slimy secretions at the surface of the epidermis which is not a homogeneous but a heterogeneous mixture of secretory substances produced by unicellular gland—the mucous cells, the club cells, the sacciform cells and the ionocytes, together with extra cellular cuticular secretions from the surface epithelial cells and exfoliated surface epithelial cells regardless of its precise biochemical nature.

Our present understanding of the physiology of mucus is limited by the lack of precise information about its chemical composition. Much of the available information on the chemical composition of the fish epidermal mucous secretions concern with histochemical and biochemical characterization of carbohydrates and amino acids by various workers. In trying to assess the functional aspect of the skin secretions it must not be forgotten that apart from the occurrence of the carbohydrate and protein moities lipids can also occur. Variation in any of these components could effect the physical and other properties of mucus.

The present investigation has therefore been designed to study lipids in epidermal mucous secretions of four fresh-water fishes *Catla catla*, *Channa striata*, *Clarias batrachus* and *Rita rita*.

Fish epidermal mucous secretion collected by wiping off the body surface using blunt edge of a scalpel and is processed for the lipid extraction using Bligh and Dyer (1959) techniques modified by Kates (1972).

Lipid protein ratio varied around 0.075 in *Catla catla*, 0.11 in *Channa striata*, 0.058 in *Clarias batrachus* and 0.068 in *Rita rita*.

Different types of neutral lipid classes and phospholipid classes are separated using one-dimentional one-step, one-dimensional two-step and two-dimensional thin-layer chromatography using various solvent systems and are identified by comparing their Rf values with that of the lipid standards and by using general and specific staining techniques. The separated lipid classes are quantified by using colorimetric techniques.

The lipid composition of epidermal mucous secretion in all the four fishes is quite similar. The neutral lipids : phospholipid ratio is around 0.75 in *Catla catla*, 0.92 in *Channa striata*, 1.1 in *Clarias batrachus* and 0.41 in *Rita rita*.

Various neutral lipid classes separated are monoglycerides, 1,2-diglycerides, 1,3-diglycerides, long-chain alcohol, free fatty acids,

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triglycerides, fatty acid methyl esters, cholesterol esters, squalene and hydrocarbons. Out of these cholesterol, triglyceride, and free fatty acids are present in relatively high amounts.

The phospholipid components separated are phosphatidic acid, phosphatidyl serine, phosphatidyl choline, lysophosphatidyl choline, phosphatidyl ethanolamine, lysophosphatidyl ethanolamine, phosphatidyl glycerol and sphingomyelin. Out of these phosphatidyl choline, phosphatidyl ethanolamine, phosphatidyl serine and sphingomyelin are present in relatively high amounts.

A series of histochemical techniques applied in an effort to localise various lipid components in various cellular constituents of the epidermis give almost similar results in all the four fishes and reveal that lipid deposits in the form of globules are absent in the epidermis. Weak histochemical reactions in the epidermis of the four fishes suggest that lipids are present either in diffused state or as an integral part of the membranous constituents of various cell types.

Lipids in mucous secretion are suggested to derive from membranous components of epithelial cells, membranous materials which bound glycoprotein vesicles in surface epithelial cells, membranes which bound mucous droplets in mucous cells and secretion filled vacuoles in sacciform cells and membranous profiles in the perinuclear areas of the club cells which are extruded along with their secretions.

Presence of lipids in epidermal mucous secretions is physiologically significant and has been correlated with the aquatic mode of life of fish.

The presence of phospholipids is correlated, to determine the viscosity of epidermal mucous secretions.

The excretion of cholesterol along with the secretions of gland cells and its property to form water-in-oil emulsion may account for the property of mucus to bind large amounts of water. This property of mucus may be of great significance for air-breathing fishes, that may facilitate in keeping the skin moist and protect it from desiccation in drying up conditions.

Relatively high amounts of fatty acids may aid in surface defence mechanism protecting the fish against bacterial and fungal attacks.

Lipids in mucus may retard rate of water exchange through the skin.

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ALTERATIONS OF ENZYMES AS A FUNCTION OF AGE : PROPERTIES OF PURIFIED LACTATE AND GLUTAMATE DEHYDROGENASE OF THE AGING RAT TISSUES

M. Prabhakaram Sup : *Dr. S. N. Singh*

There are many changes occurring during the course of aging at the molecular and biochemical levels. The most interesting out of these are the changes of biologically active molecules like enzymes. The data so far obtained on the enzymatic changes are mainly from crude tissue homogenates of aging animals. Whether the changes observed are due to structural alterations in the enzyme molecules or not, cannot be ascertained unless the studies are performed using purified enzymes from the tissues of aging animals. Hence, the present investigation is aimed to study the age-related properties of purified lacate dehydrogenase from the skeletal muscle, liver and heart and glutamate dehydrogenase from the liver of aging rats with a view if the altered and unaltered enzyme coexist in aging tissues.

Lactate Dehydrogenase

Lactate dehydrogenase (LDH) purified from young (22-w), and old (116-w) female rat tissues did not show significant age differences with respect to charge. This was supported by the study using polyacrylamide gel electrophoresis (PAGE) and ion exchange chromatography. However, H-LDH elution pattern from column and its migration on gel differs with that of muscle or liver LDH being anionic whereas it is cationic for muscle or liver LDH.

The apparent Km with pyruvate and Ki with oxalate/oxamate for H-LDH shows significant difference with M-LDH or liver LDH. Although there is no age-related variation. The ultraviolet absorption spectrum of purified LDH of liver and muscle is same for both the ages of rats.

The pH-optima for the activity of purified LDH from the liver and heart is same in young and old rats. However, pH optimum for old muscle-LDH shows a significant shift towards basic side, while young muscle-LDH has pH optimum between 5.5—7.5. Inactivation of enzyme at higher temperatures is more pronounced in case of muscle and liver-LDH as compared to heart-LDH Muscle-LDH. of old rats has shown significant differences with that of young rat muscle-LDH.

Sodium sulfite and urea, both are inhibitory for M- and H-LDH. There is difference between old and young M-LDH with respect to the

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effects of sodium sulfite and urea. It is also observed that H-LDH but not the M-LDH is sensitive to sulfite inhibition while the reverse is true for urea inhibition.

Glutamate Dehydrogenase

Glutamate dehydrogenase (GDH) was purified from the liver of immature (4–w), young (22-w) and old (116-w) female rats. The enzyme was eluted from a homogeneous peak for all the three ages of rats, with an average molecular weight of the polypeptide chain as 53,000. It is further supported by the calculated molecular weight on SDS PAGE in comparison to marker proteins. Similar values were obtained for all the ages of rats studied. The purified GDH from the liver of aging rats produced a similar ultraviolet absorption spectrum.

The apparent Km values of GDH with α-ketoglutarate, NADH, NADPH, NH_4Cl, NAD, NADP and glutamate did not show significant variation in the aging rats. There is no significant difference in the pH optimum or thermal inactivation for the liver GDH activity as a function of age.

The purified liver GDH from immature, young and old rats show induced activity with ADP/ATP but decreased activity with GDP/GTP/ITP whereas the activity of the enzyme is not affected with IDP, thus indicating the role of nucleotides regulation for the activity of glutamate dehydrogenase.

The inhibitory effects on the activity of GDH with serotonin, acetylcholine, epinephrine, norepinephrine, L-DOPA and L-aspartate is significant. There is no age-related variation in the inhibitory pattern. However, GABA and DOPAMINE did not show such inhibitory effect on the enzyme activity of immature, young or old individuals. Thus, there is a possibility of regulation of this enzyme by various neurotransmitters.

Effects of several steroid hormones has been observed on the activity of the young and old enzymes. Maximum inhibition is achieved by glucocorticoids like corticosterone and dexamethasone (synthetic) while cortisone and cortisol do not affect the enzyme even at higher concentrations. These results show that glucocorticoid inhibition is selective. Synthetic estrogen diethylstilbestrol acts as a potent inhibitor for the GDH activity in aging rats. The inhibitory characteristics did not show increase or decrease with age. Natural estrogen β-estradiol and androgens (androsterone and testosterone) have also shown the inhibitory effects on the enzyme activity in different ages of rats

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studied. Inactivation of GDH occurs with thyroid hormone (thyroxine) and it is not affected by age of the rat.

Ethanol, thiouracil and urea have inhibitory action for the activity of purified liver GDH which is almost to a similar extent for immature, young and old rats. Cyclic AMP did not affect whereas cycloheximide inhibited the liver GDH activity although at a higher concentration. However, no age dependent changes are observed.

Several metal ions are used to see their regulatory role on the activity of GDH in aging rats. Out of various ions used only silver ions have shown a strong inhibitory effect.

Inhibition by different ions in decreasing order are :

(i) Anions : Sulfite > sulfate > acetate

(ii) Cations : silver > cadmium, copper, iron and zinc> stannous > mercury > cobalt > lead > calcium> and magnesium > manganous and barium.

A significant observation is that methylated xanthines, caffeine and theophylline are inhibitory for the liver GDH of immature, young and old rats in both, forward and reverse directions of enzymatic reaction. However, theophylline inhibits the enzyme activity to a greater extent than that of caffeine. Inhibitory constants (Ki) of GDH with caffeine and theophylline are same for all the three ages of rats studied. Both the methylated xanthines are competitive with α—ketoglutarate; non-competitive with NADH, NAD and NH_4Cl; uncompetitive with glutamate. However, in presence of ADP the inhibitory effect of caffeine and theophylline is reversible. Thus, there is a possibility of same ADP site which is occupied by these inhibitors.

Thus, the properties of purified liver GDH studied with the various effectors do not reveal any structural variation and there fore, no alterations in GDH with increasing age of the rats. This may be due to its mitochondrial origin. Thus, the age-related properties of purified LDH and GDH from the rat tissues provide an evidence for the coexistence of altered and unaltered enzymes, which may be due to the post-synthetic modifications rather than sequence changes or structural alterations.

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SELF-PURIFICATION OF THE RIVER GANGA AT VARANASI

Ravi Ralph Sup : *Dr. G. P. Agrawal*

Pollution studies on the Ganga have been conducted from time to time in various important towns, consequently considerable data are available with the Indian Universities and other hydrological departments.

Domestic and industrial wastes are so indiscriminately being dumped into the Ganga at Varanasi that not only the scientific circles are alarmed but also the layman who is now well aware that unless protective measures are taken to put a curb on the ever increasing rate of waste disposal into the river, health hazards to the millions of people will be rampant.

Before any step towards the planning and subsequent set-up of the waste treatment plants at Varanasi can be taken by the Government, it would be worthwhile to study the self-purification behaviour of the Ganga without which the bulk of data on pollution studies would remain incomplete.

An effort has been made through the research presented herewith to study the self-purification of the Ganga at Varanasi and simultaneously to determine its self-purifying capacity during different months of the year.

The self-purification of a river may be defined as its natural ability to assimilate wastes by the help of biochemical activities of its micro-organisms (especially bacteria) and rebreath its natural freshness.

The following parameters were taken into consideration while studying the self-purification of the Ganga at Varanasi.

A—Physico-Chemical parameters :

1. Velocity of flow
2. Temperature
3. Depth
4. PH
5. Specific conductance
6. Dissolved oxygen
7. Biological oxygen demand
8. Ammonia (free and saline)
9. Nitrite ion
10. Nitrate ion
11. Chloride ion

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12. Sulphate ion
13. Silicate ion
14. Bicarbonate ion
15. Carbonate ion
16. Sodium ion
17. Potassium ion
18. Calcium ion
19. Magnesium ion

B—Biological Parameters

1—*Bacteria*

Presence of nitrifying bacteria, namely *Nitrobacter*, *Nitrosomonas* and *Nitrosococcus* was experimentally confirmed at stages where O_2 was used up by these autotrophs to oxidise ammonia into nitrite and nitrate.

2—*Plankton*

Out of the various zoo-plankton identified, some showed a definite defined pattern of occurance with relation to temperature, DO, BOD and the river discharge. Such species were :

Amphileptus species; *Perispira ovum*; *Actinobulina radian*; *Stentor species*; *Phacodinium species*; *Campanella umbellaria*; *Paramecium caudatum*; *Paramecium bursaria*; *Paramecium aurelia*; *Carchesium species*; *Colpidium species*; *Didinium nasutum*; *Keratella quadrata*; *Keratella hiemalis*; *Philodina species*, *Brachionus plicatilis*; *Euchlanis dilatata*; *Monomata grandis*; *Epiphanes senta*; *Branchinecta paludosa*; *Cyzicus species*; *Bosmina longrostris*.

Daphnea pulex, *Daphnea Similis*, *Cyclops insignis*, *Limnocalanus macrurus*, *Chlamydotheca speciosa speciosa*. These species were studied in greater detail with respect to the seasonal variation in their numbers and their maximum concentration in various months of the year.

Plankton Sampling

Limnological studies in India and other developing countries involving qualitative and quantitative estimation of plankton were so far being carried out by sampling the river water with the use of a simple net. It is not possible to determine the volume of water sieved during each sampling operation by using a net.

Plankton samplers used in developed countries are equipped with an electronic water flow meter to record the volume of water sieved so that two or more samplings for the planktonic concentration can be logically compared.

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Such samplers were pioneered by Juday (1926), Clarke and Bumpus (1940) and Hess (1941).

The electronic water flow meter is not available in India and other such developing countries. Thus for a sound quantitative analysis of the zooplankton, it became imperative for me to design and develop an alternative plankton sampler.

The "Limnological Plankton Sampler" as it has been named, is capable of determining the volume of water sieved during each sampling operation without the use of a water flow meter and is simple to operate. It has been used to collect data for this study and is being currently used by the Flood Forecasting and Water Resources Organisation, Department of Irrigation, Govt. of India, in sampling the Ganga waters in and around Varanasi.

Chemical Indices

Important chemical indices of the Ganga waters at Ram Nagar and Raj Ghat have been computed. These are, namely, the sodium adsorption ratio (SAR); the sodium percentage (SP); residual sodium carbonate (RSC) and the hardness number (HN).

Based on specific conductance and SAR, the water samples have been classified as C_2S_1, as per U. S. Salinity Laboratory Standard.

Oxygen Sag Curve Experiments

Oxygen Sag Curve Surveys were conducted during April-February 1978, May '79 and November '70. Each Sage Curve surve, the deaeration and reaeration coefficients and the self-purification factors were determined.

The Self-Purification Factor :

The Self-purifying factor (f of a stream is given as the ratio of its deaeration and reaeration coefficients. The values of f determined during the present study are listed below :

During February—April, 1978, the value of f was determined to be 34. B.

During May, 1979, the value of f was determined to be 22.52.

During June, 1979, the value of f was determined as 10.20.

During November, 1979, it was determined as 3.37.

The values of f, the self-purification factor lead to the fact that around Varanasi, on account of its self-purification capacity, the Ganga can still afford to bear lotion leading higher than the existing one, under similar conditions.

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This, however, provides no scope for negligence towards either efforts to limit the flow of pollutants into the river on any protective measures such as to guard the potable characteristics of the Ganga waters.

If the discharge of waste waters into the Ganga at Varanasi is continued at an ever increasing pace, it would soon result in a severe ecological imbalance of the river.

SOME PROBLEMS ON THE REPRODUCTION OF TELEOSTEAN FISH, *CHANNA PUNCTATUS* (BLOCH)

Anees Fatima Rizvi Sup : *Prof. A. G. Sathyanesan*

A. Annual cyclical changes in the ovary and testis of *Channa punctatus* (Bloch)—a histological and histochemical study

The annual cyclical micromorphological changes in the gonads can be divided into four stages, namely :—I. Resting stage which extends from late October to early January; II. Prespawning or recrudescence stage which is observed from late January to May; III. Spawning stage which is obvious from June to early September; and IV. Post-spawning stage which is evident from late September to early October. Gonadal growth coincides with the gradual increase in water temperature and day length. Onset of monsoon is an essential triggering factor for the initiation of spawning activity in this species.

Resting stage ovary contains nests of primordial germ cells and stage-I oocytes. In stage-I oocytes nucleolar numbers increases and yolk nucleus (YN) appear in the cytoplasm close to the nuclear membrane. YN is sudanophilic and gives positive reaction to Golgi technique and alkaline phosphatase test but acid phosphatase could not be identified. Occasionally few PAS-positive granules could be seen in the core of the YN. Follicular wall which is not well differentiated exhibits moderate G-6-PD activity; but $\triangle^{5}$-3β HSD is absent. During early prespawning phase stage-II oocytes increase in size and large number of peripheral cytoplasmic vacuoles appear. In the late stage-II oocytes deposition of yolk is initiated and the thecal, granulosa layers and the vitelline membrane are progressively differentiated. All the three types of yolk material could be identified. G-6-PD activity increased in the follicular layer while reaction for $\triangle^{5}$-3-β HSD was very weak. During spawning phase, stage-III matured oocytes were seen. The thecal and

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granulosa layers exhibited strong G-6-PD and $\triangle^{5}$-3β HSD activity. In the postspawning period the ovary contained post-ovulatory follicles, relict oocytes and resting stage-I oocytes.

During all the growth stages of the ovary, varying number of oocytes were aborted and resorbed. Initially in all the atretic oocytes the nucleus degenerates and subsequently granulosa and thecal cells exhibit hypertrophy and hyperplasia. Often the vitelline membrane, separates off from the follicular wall, breaks or swells and disintegrates. The yolk globules and the cytoplasmic contents liquefy and the invading follicular components engulf them. Finally, the atretic oocyte is reduced into an irregular group of cells with brown pigment masses. The follicular wall of the atretic oocytes exhibited moderate G-6-PD activity whereas $\triangle^{5}$-3β HSD was almost absent. Alkaline and acid phosphatase activity could be demonstrated for a long time during the resorption process.

In the resting stage testis, seminiferous tubules resemble cords made up of primary spermatogonial cells. Their interstitium is thick and sudanophilic. The Leydig cells are inactive; G-6-PD reaction is more intense in the interstitium than in the tubular walls and $\triangle^{5}$-3β HSD activity is not detectable. During the prespawning stage, both primary and secondary spermatogonia and spermatocytes are found. During the late stage-II testis, few tubules with some groups of sperms were also seen. The Leydig and lobule boundary cells showed intense reaction to sudan black B, alkaline and acid phosphatases and G-6-PD. During spawning stage the intertubular space becomes narrow and the lumen of the tubules are filled with sperms. Leydig cells exhibited positive reaction to alkaline and acid phosphatases, and G-6-PD and $\triangle^{5}$-3β HSD activity. Although the lobule boundary cells are distinctly seen, they are devoid of $\triangle^{5}$-3β HSD activity. During post-spawning stage the seminiferous tubules become empty. The Leyding and lobule boundary cells become small and less active.

While examining the section of the testes of over 400 *C. punctatus* in relation to various investigations, four specimens exhibited scattered resting stage oocytes. As no further growth stage was noticed, they may be considered as occasional hermaphroditism and those germ cells may abort subsequently.

B. Histomorphology of the gonadal cysts with a note on a parasitized testis

While examining the sections of few hundreds of gonads of *C. punctatus* and *C. auratus* in relation to various studies, three ovarian

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cysts were noticed in the former and two in the latter. In *C. punctatus* cysts were more common in the testes than in the ovary. Ovarian cysts may be small or large enough to occupy 1/3rd of the ovary. Outer layer of the vascular cyst wall is fibrous, with scattered spindle shaped nuclei and the inner layer seems to be homogeneous. Few stage-I oocytes were occasionally seen inside the cyst wall. However, only those oocytes lying in close contact with the cyst were degenerated whereas others were apparently normal.

The occurrence of cystic tumours in the testes of *C. punctatus* was comparatively more common and sometimes as many as 15 to 20 cysts could be counted in a single section. The cyst which may be inter or intratubular has a definite multilayered wall with spindle shaped cells. The cystic lumen may be filled with homogeneous or amorphous substance. As in the case of the ovary, in the testes also no abnormality was seen in the unaffected regions. However, the causative factors for such tumours are yet to be identified. In one of the hundreds of testes examined a large trematode cyst was noticed. Under such parasitized condition also, the germ cells away from the cyst are apparently normal.

Chapter II

A. Circannual histological and histochemical changes in the pituitary gland of *Channa punctatus* (Bloch), and their correlation with the gonadal cycles

The pituitary of C. punctatus is devoid of a distinct stalk and is closely applied to the floor of the brain through two short infundibular processes. Eight endocrine cell types were demonstrated in the adenohypophysis. The rostral pars distalis (RPD) is made up of three cell types, namely, the lead haematoxylin positive type-1 cells, the corticotrophs (ACTH); type-1 acidophils (ACl), the lactotrophs, stainable with OG, erythrosin and acid fuchsin and the cyanophils type-I (Cyl) which are the thyrotrophs. Cyl are fewer in number and are readily stained with PAS, AB, AF, AT and aniline blue.

The proximal pars distalis (PPD) consists of acidophilic type-2 cells (AC2), the somatotrophs, cyanophils type-1 (Cy1) the thyrotrophs and cyanophils type-2 (Cy2) the gonadotrophs. Somatotrophs are stained with orange-G, erythrosin, acid fuchsin and Baker's acid hematein. As the thyrotrophs and gonadotrophs reacted in the same manner to all the techniques used, they can not be identified without adopting experimental procedures. The thyrotrophs of the RPD and

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PPD exhibited increased activity in response to thiourea and TSH treatments. Those cells that increased in number and exhibited hypertrophy, degranulation and vacuolization during spawning phase and showed correlative cyclical changes with the gonadal cycles are the gonadotrophs.

The pars intermedia contains two cell types, the PbH-positive type-2 (PiPbH) and the PAS-positive type-3 cyanophils (Cy3 or PIPAS).

B. Experimental Studies

Long term thiourea treatment induced hypertrophy, and hyperplasia of the follicular cells of the thyroid and caused retardation of gonadal recrudescence. Besides thyrotrophs, the lactotrophs, corticotrophs and the PIPAS cells were also activated to varying degrees in thiourea treated fish. The short term TSH administration also caused comparable but less pronounced changes.

Reserpine and serotonin administration resulted in darkening of the skin. Serotonin induced degeneration of the maturing and matured vitellogenic oocytes. In the reserpine and serotonin exposed fish, the corticotrophs were degranulated. In response to reserpine treatment PIPAS and PIPbH cells exhibited marked degranulation whereas serotonin activated only the PIPbH cells.

Exposure to endosulfan which is an organochlorine insecticide, caused marked retardation of ovarian recrudescence. The corticotrophs, PIPAS and PIPbH cells exhibited hypertrophy and degranulation.

Among the several hundred fish examined in one control specimen one-third of the PPD was seen pushed into the third ventricle. However, there was no obvious change in its structure and function.

C. Micromorphology of the adenohypophysial cystic cavities in *Channa punctatus* (Bloch).

In *C. punctatus*, pituitary cysts of varying shape and size are fiarly common and are largely restricted to the proximal pars distalis (PPD). These cysts seem to originate as small intercellular spaces which enlarge at the cost of the surrounding cells. As the small cavities enlarge, adjacent ones tend to merge together forming larger cysts. Although they are lined by both cyanophils and acidophils; during the spawning phase the cyanophils preponderate. Light microscopical observation did not reveal the presence of any definite internal or external limiting membrane or wall. They are highly vascular like any other part of the

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pituitary and sometimes blood vessels even project into the cysts. The lumen contains homogeneous or granular material. Some may have PAS-positive globules, phagocytes, free blood cells, viable and degenerating gland cells. Occasionally large chromophobes were also seen projecting into the lumen.

STUDIES ON THE EXPRESSION OF HEAT SHOCK GENES IN *DROSOPHILA*

Ajit Kumar Singh Sup : *Dr. S. C. Lakhotia*

A small number of genes in all cells from bacteria to man respond to heat and certain other conditions of stress. These genes are widely known as heat shock genes. The present thesis contains results of studies of the expression of heat shock genes in *Drosophila* with particular reference to the evolutionary conservation and regulation of one of the heat shock genes, the 93D locus of *D. melanogaster*. Of the nine heat shock loci known in *D. melanogaster*, the 93D locus is unique in view of its several already known unusual features.

Observations of conservation of the 93D heat shock locus in different species of *Drosophila* are presented in the first part of this thesis. The species of *Drosophila* which have been studied are *D. ananassae*, *D. kikkawai*, *D. nasuta* and *D. hydei*. Larval salivary glands of these *Drosophila* species were subjected to heat shock (37°C for 30 min) or were treated with benzamide (1 mg/ml) or with vitamine-B_6 (2.5×10^{-6}M) and the induction of puffs was studied with the help of puff size measurement and/or ^{3}H-uridine autoradiography. Six to nine puffs have been found to be induced after head shock in salivary gland polytene nuclei of different species of *Drosophila*. The most significant observation of the present study has been that irrespective of phylogenetic relationships, one and the same heat shock puff in each species (viz. 2L-2C in *D. ananassae*, E-11B in *D. kikkawai*, 2-48C in *D. hydei* and 2R-48A in *D. nasuta*) is selectively inducible by benzamide as well as by vitamine-B_6 (except in *D. melanogaster* which, for some unknown reasons, is insensitive to vitamine-B_6). Thus, although as is known from earlier observations, that the 93D locus differs from other heat shock loci in several ways and its transcription products perhaps do not translate into protein, yet this locus is conserved in different species of *Drosophila*.

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The second part of the thesis contains studies on aspects of regulation of heat shock puffs, specially of the 93D or 93 D- like puff in *Drosophila* species. This study has been divided into three chapters.

The first chapter of this part deals with nature of the 93D or 93D-like puff inducing factor/s present in homogenate of heat shocked cells. Salivary glands from late third instar larvae of *D. melanogaster* or *D. hydei* were incubated in a homogenate of heat shocked larvae or salivary glands of *D. melanogaster* or *D. hydei* or *D. nasuta*. The homogenate of heat shocked cells of a given species is found to specifically induce the 93D or 93D-like puff (viz. 2-48C in *D. hydei* or 2R-48A in *D. nasuta*) in autologous but not in heterologous salivary glands. Thus it seems that factor/s responsible for 93D or 93D-like puff induction present in the homogenate of heat shocked cells is/are species specific. It is further observed that homogenate of heat shocked *D. hydei* larvae looses its 2-48C puff inducing activity after being preheated at 80°C or at 100°C whereas *D. melanogaster* heat shocked larval homogenate heated to 80°C or 100°C retains its 93D-inducing activity. Thus the factor/s responsible for 93D induction present in the homogenate of heat shocked *D. melanogaster* cells is/are heat stable while 2-28C inducing factor of *D. hydei* is not.

The second chapter of part II of the thesis includes observations on the effects of several microtubule (MT) poisons on heat shock puffs since colchicine has been earlier reported to specifically induce the 93D puff of *D. melanogaster*. Salivary glands of *D. melanogaster* larvae were treated with several different microtubule poisons to ascertain whether the colchicine induced activity of the 93D puft is related with microtubule disruption. The different MT poisons used are : Cold shock (4°C or 8°C), Podophyllotoxin, Chloral hydrate, Diamide, Griseofulvin, Vinbalstin and Nocodazole. It is seen that cold shock induces the 93D puff but none of the other MT poisons induce the 93D or any other heat shock puff. Thus it seems that 93D-inducing activity of colchicine is not related to its microtubule disruption property.

The third chapter contains studies on heat shock puff induction in *D. melanogaster* larvae reared at 10°C to examine the effect of growth condition on heat shock gene expression at transcriptional and translational levels. Salivary glands of cold-reared larvae were subjected to heat shock at 37°C or were treated at 10°C or at 24°C with benzamide (1 mg/ml), colchicine (100 μg/ml) or Na-Cacodylate (10-15 mg/ml). It is observed that in heat shocked cells of cold-reared larvae, the 93D puff is not induced while the 87C is nearly twice as active as its duplicate locus at 87A. Interestingly, other specific inducers of 93D puff,

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like benzamide and colchicine also fail to induce the 93D puff. Na-Cacodylate, an arsenic compound, mimics the heat shock response at 24°C, although in 10°C reared larval glands, the 93D is not induced by Na-Cacodylate also. It is significant that Na-Cacodylate treatment does not cause the 87A and 87C loci to be unequally active in cold-reared larvae. However, while 93D puff is insensitive to its specific inducers, warm-shock (incubation of salivary glands of 10°C grown larvae at 24°C) causes specific activation of the 93D puff. Although, colchicine is reported to modify the heat shock induced activity in 20°-24°C reared larvae it has no effect on heat shock gene expression after heat shock or Na-Cacodylate treatment in cold-reared larval glands. Thus from these observations, it appears that the regulation of 93D puff is independent of other heat shock loci and depends upon the developmental history of the organism. These observations further confirm the earlier suggestions that inhibition of 93D activity during heat shock causes the 87A and 87C loci to be unequally induced. The pattern of heat shock protein synthesis after heat shock or Na-Cacodylate treatment is also found to be different in cold-reared larvae than in warm-reared larvae, specifically with respect to the synthesis of low mol. wt. heat shock polypeptides (HSPs) viz. 27, 26, 23 and 22 KD. The synthesis of 23 KD HSP has not been observed, neither in control nor in heat shocked cold-reared larval glands, while the same is synthesized in significant amounts in Na-C treated glands. From these results it seems that although mRNAs for the low mol. wt. HSPs are transcribed from the same 67B puff, their translation is not co-ordinated.

ROLE OF STEROIDAL HORMONES IN ANNUAL GONAD DEVELOPMENT CYCLE OF MALE BIRDS

Vinod Kumar Singh Sup : *Dr. S. C. Lakhotia*

The present dissertation includes studies to determine the role of steroidal hormones (testosterone) and corticosterone) in annual gonad development cycle of migratory and photoperiodic Red-headed bunting. *Emberiza bruniceps* and non-migratory, non-photoperiodic Red munia, *Estrilda amandava*. These studies have been divided into eight sections :

Section I

This section comprises of a brief review of the literature and a general introduction.

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Sectiou II

It includes a general description of materials and methods utilized in the present dissertation.

Section III

Seasonal changes in body weight, testis volume/weight, diameter of seminiferous tubule, vas deference weight adrenal weight and width of adrenocortical cord of Red-headed bunting, *Emberiza bruniceps*, were noted over twenty months period.

(1) Body weight and testis activity of birds started increasing almost parallel with increasing daylength during March-April, but attained peak during May and June respectively.

(2) Body weight of birds again increased after fall migration (during November to January).

(3) Adrenal cortex appeared active throughout the year but became hypertrophied during April and September, coinciding with the timing of spring and fall migration respectively.

Section IV

Effect of long term and short term administration of different doses of testosterone on body weight and testicular activity of Red-headed bunting was examined :

(1) Administration of different doses of testosterone (0.01 μg, 0.10 μg, 2.0 μg, and 8.0 μg) in Red-headed bunting over long duration (A : December 1978 to August 1979; B : April 1979 to August 1979; and C : August 1979 to January 1980) did not affect body weight but with 0.01 μg and 0.10 μg dose levels testis activity was first suppressed and then stimulated during progressive phase of sexual cycle.

(2) Testosterone at 2.0 μg and 8.0 μg levels were almost ineffective.

(3) Higher doses of testosterone (100 μg, 180 μg, and 500 μg) were injected during May to August. During the experiment following 100 μg testosterone administration. Body weight was maintained but testis activity was decreased. Testosterone at 500 μg dose level was able to maintain testis activity but rate of regression of body weight was only partially reduced during the course of study.

(4) On the basis of long term study three most effective doses (0.01 μg, 0.10 μg, and 100 μg were choosen and injected in birds during every month of the year. Birds were killed after one month of treatment. Response of body weight and testis to different doses of testosterone was

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almost similar as observed in the long term study, viz., 0.01 μg and 0.10 μg first inhibited (preparatory to early progressive) and then stimulated (late progressive phase of sexual cycle) the testis activity. Testosterone at 100 μg dose level suppressed and/or inhibited the testis activity depending upon the sexual phases of gonad development cycle.

Body weight, however, was increased during progressive phase (March to April) following administration of 100 μg of testosterone only.

(5) Very high doses of testosterone were injected during different phases of gonad development cycle. Body weight was not affected but testis activity was stimulated and/or maintained following high doses of testosterone administration during all phases of gonad development cycle.

(6) During August to September high doses proved fatal and birds did not survive for even ten days. However, whole body oxygen consumption and blood variables were studied after testosterone administration which indicated that oxygen uptake was increased but hemoglobin content and red blood corpscles were not significantly affected.

Section V

Different doses of corticosterone were injected during different months of the year.

(1) Corticosterone delayed the testicular activity for some time during progressive phase and decreased body weight of Red-headed bunting during regressive and quiscent phase of gonad development cycle.

(2) Corticosterone when injected in light stimulated birds (15 L : 9 D) almost similar results were obtained as was observed under NDL. It delayed the testicular development for fifteen days when injected on zero day or 10th day of photostimulation and after that period it had no effect. Further body weight increase was suppressed and rate of regression was increased following corticosterone administration on zero day and 30th day respectively.

Section VI

To secure detail and complete information on the effects of different doses of testosterone on body weight and testis activity cycles a non-migratory and almost non-photoperiodic bird, Red munia was selected and injected with testosterone during different phases of sexual cycle

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both over long and short durations. Changes in LH dependent plumage colour were recorded.

(1) During long term study (October 1979 to October 1980) administration of testosterone (0.01 μg, 0,10 μg, 0.50 μg, 5.0 μg, 50 μg, 100 μg, 250 μg) led to suppression of the increased body weight and testis activity during progressive phase of sexual cycle.

(2) Lower doses (0.50 μg and 5.0 μg) were ineffective during late progressive phase of sexual cycle, but higher doses (50 μg, 100 μg, and 250 μg) did not permit the gonad for full development.

(3) Comparatively higher doses of testosterone (5.0 μg, 50μg, 100 μg, 250 μg) led to regeneration of melanolytic plumage which is not generally found in normal birds.

(4) During short term (one month) experiment performed throughout the year with most effective doses of testosterone (0.5 μg, 5.0 μg, and 50 μg) almost similar results were obtained as was observed during long term study. Testosterone at 0.5 μg and 5.0 μg level suppressed the testis activity during progressive phase (May-June) and after that produced no effect. Testosterone was able to produce inhibition on testis activity at 50 μg dose level during late progressive phase but during breeding phase (September-October) had no effect. Only 100 μg of testosterone was able to inhibit the fully developed testis of Red munia.

(5) In contrast to Red-headed bunting lower doses (0.01 μg and 0.10 μg) did not produce stimulatory effect in Red munia.

(6) Higher doses of testosterone also stimulated and/or maintained testicular activity of Red munia. No mortality was recorded following high doses of testosterone administration in Red munia.

(7) High doses of testosterone produced melanolytic plumage.

(8) Since inverse thyroid gonad relationship is evidently demonstrated in Red munia, therefore, both thyroxine and testosterone were injected in sham-operated, thyroidectomized and orchidectomized birds during regressive phase of gonad development cycle to study the effect of these hormones on body weight, testis activity and feather colour.

(9) High dose of l-thyroxine was more effective than low dose in decreasing body weight and testicular activity of Red munia. Further, while low dose of testosterone was almost ineffective, high dose produced effect similar to that of produced by low dose of thyroxine.

(10) Melanolytic plumage was regenerated following testosterone and thyroxine administration.

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Section VII

Corticosterone did not produce any effect on decreasing body weight and testis activity of Red munia. The colour of the feather was also not affected by corticosterone treatment.

On the basis of above studies it was concluded that :

(i) Body weight and testis activity run parallel with increasing daylength. Body weight decreases (May) prior to decrease in testes activity (June) indicating that "Metabolic refractoriness" preceeds the "Gonadal rafractoriness" in Red-headed bunting.

(ii) Body weight cyclicity of migratory Red-headed bunting is different from that of temperate zone migrants in the sense that body weight increases during spring migration (April) and attains peak during breeding (May) period. Further it increases during post-fall migration (November to January) after reaching a trough during post-breeding period (regression phase).

(iii) Graded doses of testosterone are reqired to suppress or inhibit the gradually increasing activity of neuroendocrine system indicating that activity of neuroendocrine system changes with changing environment and consequently its sensitivity to gonadal hormones may also change.

(iv) Although, in general, testosterone produces negative feedback effect, very small doses of this hormone may also produce positive feedback during progressive phase of gonad development cycle.

(v) Same amount of hormone may produce different effects during different phases of gonad development cycle.

(vi) Testosterone at 100 μg dose level can suppress or inhibit the testis activity while at 1000 μg dose level can stimulate and/or maintain the testis activity in any phase of gonad development cycle of birds.

(vii) Response of neuroendocrine system to gonadal hormones may be influenced by thyroidal hormones.

(viii) Sensitivity of the vas deference to testosterone changes with changing phases of gonad development cycle.

(ix) Body weight cycles of Red-headed bunting and Red munia are not much influenced by testosterone.

(x) Thyroxine is more potent inhibitor of body weight and testis activity of Red munia than testosterone.

(xi) Testosterone may change the different pathways of melanin synthesis resulting in production of melanolytic feathers in Red munia.

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(xii) Similar to testosterone thyroxine may also influence the metabolic pathways of melanin synthesis in Red munia.

(xiii) In Red-headed bunting cortical hormones are probably mainly involved with migration, however, it can delay the reproductive processes for some time during adverse conditions.

(xiv) Cortical hormones are probably not primarily involved in body weight and testis activity of Red munia.

(xv) It seems that adrenocortical hormone is not influencing the metabolic pathways of melanin synthesis because the plumage colour remained unaffected following corticosterone administration.

We hope that the results of these studies would contribute to a better understanding of the role of steroidal hormones in modulation of annual body weight variation and activity of hypothalamo-hypophyseal-gonadal axis in migratory/non-migratory and photoperiodic/non-photoperiodic birds. Similar studies in temperate zone birds would be interesting.

EFFECT OF DIFFERENT POTENCIES OF CAULOPHYLLUM (A HOMOEOPATHIC DRUG) ON REPRODUCTION IN RATS

Anil Kumar Srivastava Sup : *Dr. (Mrs) K. C. Sarkar*

Demographers, economists and politicians are equally aware of the dismal picture of the future of the developing countries, if population growth continues unabated. This is because the earth's resources for providing the basic necessities of life such as food, clothing and shelter are getting impoverished. Merilyn Merrit (1983) said that "most developing countries have come to recognize that population growth is indeed a problem closely related to development." It is a general feeling that if any quality has to improve then, population growth has to be curbed. Many of the contraceptive methods in vogue, are not acceptable to large majority of the people due to unpleasant side effects produced by them or the necessity to undergo surgery or visit a clinic. Further as Briggs and Briggs (1978) pointed out that "inspite of two decades or more researches, currently there is a great demand for readily acceptable and safe oral contraception and other sterilization methods which could be at the disposal of the family planning units." Unless a greater variety of contraceptives are available a large propor-

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tion of the population especially in the developing countries will not easily take to birth control. Therefore, this study was undertaken. The drug *Caulophyllum* was found to possess estrogenic properties (Chandrasekhar *et al.*, 1974). Estrogens are known to prevent pregnancy if administered at the appropriate time (Chang, 1965). These factors together with the established fact that *Caulophyllum* is a non-steroid, possessing estrogenic properties were the main guiding factors to undertake this piece of investigation.

The study mainly centres around the effect of the drug on the gonads, uterii and particular region of the arcuate nucleus.

The thesis is divided into four chapters.

In chapter one the effect of 30, 200, 10,000 and CM potencies of *Caulophyllum* on the uterii, ovaries and arcuate neurons of phypothalamus of normally cycling rats after hrs. 2, 24, 48, 72 and 7 days of drug administration are assessed histomorphologically. The assessment showed that the drug *Caulophyllum* brought about quantitative increase of uterine tissues, increase in uterine weight, accumulation of fluid, hyperplasia and hypertrophy of luminal epithelial cells and increase in height of endometrium. On the other hand the drug brought about degenerative changes in the ovaries such as weight decrease, decrease in number and mean diameter of corpora lutea, increase in the number of atretic follicles, cells of corpora lutea with vacuoles and pyknotic nuclei and blebbing of cytoplasm. Arcuate neurons were comparatively more granulated and deeply stained than in the controls. The data, thus, brings out the estrogenic properties of drug *Caulophyllum*. Further, the negative response of the arcuate neurons helps to establish the mode of action of the drug.

In chapter two the responses made by the uterii and arcuate neurons of spayed rats to a known estrogen, ovocyclin (estradiol benzoate) and *Caulophyllum* are compared. A close assessment revealed that ovocycline and *Caulophyllum* brought out parallel reactions in the uterine tissues. Thus, there was weight increase, the DNA synthesis was more in epithelial cells of treated groups as the mitotic divisions are more in the epithelia cells. The arcuate neurons showed a decrease in nuclear-neuronal volume. They were more granulated and darkly stained. Such a comparison, between the drug and ovocycline on the uterii and arcuate neurons helps to confirm that the drug *Caulophyllum* possesses distinct estrogenic properties.

In chapter three, bioassay using homogenate of the arcuate region of ovariectomized and drug administered rats on the uterii and ovaries

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of normally cycling rats was done. The rats were ovariectomized and after a lapse of 5 days vehicle/drug was administered and sacrificed after hrs. 2, 24, 48 and 72. Their hypothalamii were removed and frozen. The homogenate was prepared from 100 μ of tissue taken from IIIrd division of arcuate nuclei, in 1.0 ml. of physiological saline and was injected intramuscularly to normally cycling rats at proestrus. Assessment of the results were made after 24 hrs. Histological picture of the uterii showed that the homogenate brought about increase in uterine weight, increase in the height of luminal epithelial cells and endometrium. Mitotic divisions were more in the treated groups. Ovaries of the treated groups in many cases showed retardation of maturing ova and general degeneration. This is yet another proof that *Caulophyllum* possess estrogenic properties.

Estrogens are known to bind themselves to the receptor sites in several regions in the brain in addition to the neurons in the conventional hypophysiotropic area. In order to have additional proof of the drug's estrogenic properties, bio-assay of a particular region of cerebral cortex was designed. Thus, the cerebral cortical, area in the epithalamus lateral to the pineal body, of ovariectomized and drug administered rats were prepared and injected into normally cycling rats. The responses made by the uterii and ovaries were studied. The responses made were very much similar to those brought about by estrogen administration such as increase in uterine weight, increase in height of luminal epithelial cells and endometrium. The ovaries tend to be degenerative. These studies also help to conclude that the drug is estrogenic.

In chapter four the effect of *Caulophyllum* on the early pregnancy were studied. The different potencies of *Caulophyllum* were administered precoitus to female rats only and they were allowed to mate with coeval males. If the sperms were detected the following morning then the drug was administered again and thereafter after hrs. 2, 8, 12, 24 and 48. Laparotomies were performed on days 6, 10, 17 and 21 of pregnancy for macroscopic assessment. On day 6 of pregnancy in normal controls, blastocysts were present while in treated groups only black spots (freely floating blastocysts) were found, in a few cases even black spots were absent. On day 10 of pregnancy, laparotomies revealed that in normal controls, embryos were developing while in the treated groups even the black spots had disappeared and in most of the cases uterii were filled with fluid. On day 17 of pregnancy laparotomies showed that in normal controls, fully developed embryos were present while in the treated groups there was no sign of pregnancy.

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On day 21, the normal controls delivered pups while there were no signs of pregnancy in the treated groups. Histological pictures of the uterii of the drug treated groups on days 6, 10, 17 and 21 of presumed pregnancy revealed, them to be in the estrous condition with the luminal epithelium hypertrophied and "sloughing off." Thus it brings about that the drug *Caulophyllum* being estrogenic prevents implantations.

The four sets of experiments shows clearly that *Caulophyllum* in its 30, 200, 10,000 and CM potencies possesses estrogenic properties. The responses made by the uterii, ovaries and hypothalamic arcuate neurons confirm to the action of endogenous as well as known exogenous estrogens (ovocycline).

The investigation on pregnancy goes to prove beyond doubt that its estrogenic properties may be utilized for benefit of fertility control.

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